228. *Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part V.*[1] *Kinetics, Stereochemistry, and Mechanism of Anion-catalysed One-alkyl Mercury-exchange Reactions.*

By H. B. CHARMAN, E. D. HUGHES, SIR CHRISTOPHER INGOLD, and H. C. VOLGER.

Mercury-exchange between alkylmercuric and mercuric salts, as followed through transfer of radioactivity, is catalysed by anions which co-ordinate strongly with mercury. This is shown for iodide, bromide, chloride, and acetate, as catalysing anions, the catalysis diminishing in this order, and for methyl and s-butyl as alkyl groups. A kinetic study showed that, in general, two catalytic processes are concurrently at work; that both are one-alkyl electrophilic substitutions, bimolecular apart from the catalysis; but that in one, an extra anion is taken into the reacting system, and that in the other two extra anions are so included. These two catalytic processes can be separated in favourable cases, and, this having been done, it was shown, by work with optically active s-butylmercuric salts, that in each process stereochemical configuration is fully preserved. It is argued that both processes have cyclic transition states, and, indeed, are forms of the internal mechanism of electrophilic substitution, S_Ei, contemplated in Part I, and now observed for the first time.

(1) *The Basic Observation.*—The form of one-alkyl mercury-exchange here to be described is new, except for the brief mention of it in Part IV [1] Section 4, and the mention of its use to prepare a doubly-labelled alkylmercuric salt in Part III,[2] Section 6a. The basic observation is that, when, in a one-alkyl mercury-exchange with anions which co-ordinate well with mercury, a common-anion alkali-metal salt is added, the exchange undergoes an acceleration far beyond the scope of any medium effect. For example, the mercury-exchange between methylmercuric bromide and mercuric bromide, each, say, in 0·1M-concentration in ethanol, is accelerated by comparable concentrations of lithium bromide by factors of the order of 100. This is no normal salt-effect, analogous, say, to that of lithium nitrate or lithium perchlorate: we designate it as a catalysis, implying that a new mechanism has intervened. We have found such catalysis in one-alkyl mercury-exchanges with iodides, bromides, chlorides, and even acetates; and with methyl and s-butyl, as examples of alkyl groups. We report below the kinetics and stereochemistry of this catalysed reaction.

(2) *Kinetics of the Anion-catalysed One-alkyl Substitution.*—The kinetics have been studied most fully in the example of the following exchange reaction in ethanol at 60°:

$$\mathrm{MeHgBr} + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \xrightleftharpoons{\mathrm{LiBr}} \mathrm{Me}\overset{*}{\mathrm{Hg}}\mathrm{Br} + \mathrm{HgBr_2}$$

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[1] Part IV, Hughes, Ingold, Thorpe, and Volger, preceding paper.

[2] Part III, Charman, Hughes, Ingold, and Thorpe, *J.*, 1961, 1121.

where the asterisk denotes a label of radioactivity, that of ^{203}Hg. The rate data are in Table 1. The first-order rate-constant of label-transfer, k_1^{Hg}, is an experimental result, independent of any hypothesis concerning the kinetic form of the substitution; and so is the rate of exchange, $k_0^{Hg} = k_1^{Hg}ab/(a + b)$, where a and b are the concentrations of mercuric bromide and methylmercuric bromide, respectively. From these experimental constants, we can derive various rate-constants of substitution, according to our hypothesis of its kinetic form; but in fact we tabulate only the second-order rate-constant of one-alkyl substitution, $k_{2c}^{(1)} = k_0^{Hg}/ab$, calling it $k_{2c}^{(1)}$ (obs.), to distinguish it from the quantities, called $k_{2c}^{(1)}$ (calc.), which are calculated from a formula, derived below from a theory of the mechanism of the catalysis.

Several general points are apparent. First, the second-order rate-constant of one-alkyl substitution, $k_{2c}^{(1)}$ (obs.), is nearly invariant with changing concentration of methylmercuric bromide, when the other concentrations are kept constant. So, indeed, would be the first-order rate-constant of one-alkyl substitution, $k_1^{(1)} = k_0^{Hg}/b$. But since the unimolecular mechanism, corresponding to that constant, is excluded by the stereochemical results reported in Section 4, we do not consider the first-order constant further. The second-order constant of two-alkyl substitution, $k_2^{(2)} = k_0^{Hg}/b^2$, is not invariant with any concentration, and hence two-alkyl substitution is excluded. Moreover, since we know [3] that two-alkyl substitution is strongly retarded by lithium bromide, that process is excluded by the catalysis. Neither, therefore, shall we consider that constant any further.

TABLE 1. *First-order rate-constants of label-transfer* (k_1^{Hg} *in* sec.$^{-1}$), *rates of exchange* (k_0^{Hg} *in mole* l.$^{-1}$ sec.$^{-1}$), *and second-order constants of one-alkyl substitution* [$k_{2c}^{(1)}$ (obs.) *in mole*$^{-1}$ l. sec.$^{-1}$] *by mercuric bromide* (*concentration* a) *in methylmercuric bromide* (*concentration* b), *under catalysis by lithium bromide* (*concentration* c), *as radiometrically determined by mercury-exchange in ethanol at* 59·8°.

[The radioactivity of ^{203}Hg was initially in the mercuric bromide. Concentrations and rate-constants are corrected for thermal expansion of the solvent. As to $k_{2c}^{(1)}$ (calc.), see Section 5.]

Run	a (M)	b (M)	c (M)	$10^6k_1^{Hg}$	$10^7k_0^{Hg}$	$10^5k_{2c}^{(1)}$ (obs.)	$10^5k_{2c}^{(1)}$ (calc.)
63, 69	0·095	0·095	0·000	0·92	0·44	0·49	—
55	0·095	0·095	0·035	24·3	11·6	12·8	12·9
76	0·095	0·095	0·065	40·8	19·4	21·5	23·9
52	0·095	0·095	0·105	74	35·2	39	40
53	0·095	0·095	0·161	131	52	69	68
62	0·095	0·095	0·203	167	79	88	89
67	0·095	0·095	0·203	171	81	90	89
70	0·095	0·095	0·271	230	109	121	123
59	0·095	0·095	0·311	277	132	146	143
61	0·176	0·095	0·193	141	87	52	44
68	0·252	0·095	0·206	125	86	36	29
64	0·291	0·095	0·205	127	91	33	25
66	0·095	0·158	0·204	190	112	75	89
69	0·095	0·190	0·214	216	137	76	94

Secondly, as can be seen from the plot in the Figure, the second-order rate-constant of one-alkyl substitution, $k_{2c}^{(1)}$ (obs.)—the constant itself, not its logarithm, as would be more relevant to the consideration of normal salt-effects—increases linearly with the concentration of lithium bromide over considerable ranges, when the other concentrations are kept constant. Moreover, the gradient of linear increase becomes larger rather sharply when the concentration of lithium bromide exceeds that of mercuric bromide. Thirdly, when this is so, then, for a constant concentration of lithium bromide, the second-order constant, $k_{2c}^{(1)}$ (obs.), becomes much reduced on increasing the concentration of mercuric bromide. It seems also to be reduced, though only slightly, on increasing the concentration of methylmercuric bromide.

Though we shall develop the theory of the catalysis in more detail in Section 5, the

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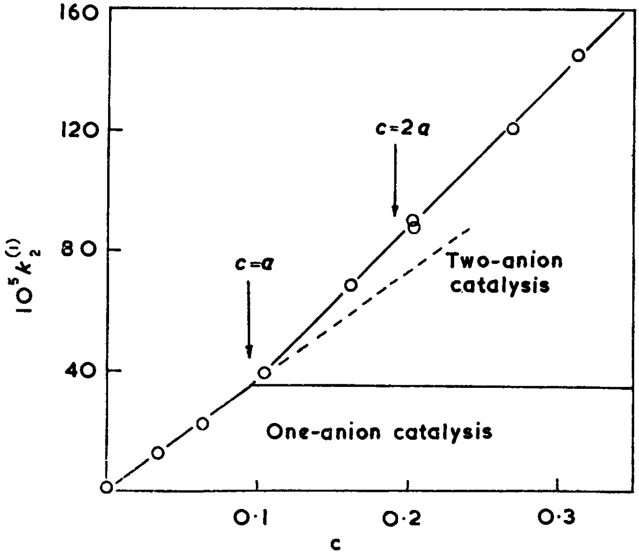
[3] Charman, Hughes, and Ingold, *J.*, 1959, 2530.

general nature of what is happening will already be obvious. As long as the concentration of lithium bromide is less than that of mercuric bromide, we observe a single catalysis, depending on a transition state of reduced free-energy; and this transition state could be, and no doubt mainly is, produced from the molecule MeHgBr and the anion $HgBr_3^-$, the latter preformed nearly stoicheiometrically from $HgBr_2$ and Br^-. When the concentration of lithium bromide exceeds that of mercuric bromide, then a second and superposed catalysis comes under observation, involving a transition state of slightly lower free-energy still; and this second transition state could be, and may largely be, produced from the two anions $HgBr_3^-$ and $MeHgBr_2^-$ provided that, after preformation of the former is complete, that of the latter proceeds to only a small equilibrium extent.* It is convenient to name these two types of catalysis " one-anion " and " two-anion " catalysis.

Dependence of second-order rate-constants of one-alkyl substitution, $k_{2c}^{(1)}$, by mercuric bromide in methylmercuric bromide in ethanol at 59·8°, *on the concentration* (*c*) *of added lithium bromide, the concentrations* (*a and b*) *of the mercury-exchanging substances being* 0·095M.



The curve is that of equation (i), p. 1148, *with* $10^5\kappa_1 = 35$ *mole*$^{-1}$ *l. sec.*$^{-1}$ *and* $10^5\kappa_2 = 500$ *mole*$^{-2}$ *l.*^{2} *sec.*$^{-1}$. *The positions marked* $c = a$ *and* $c = 2a$ *are where breaks should occur according to different assumptions that might be made for the purpose of deriving a theoretical equation* (*cf. Section* 5).

(3) *Kinetics*: *Generalisation to Other Anions and Another Alkyl Group.*—It was obviously necessary to establish the scope of anion catalysis, and to confirm, if possible, its suspected dependence on the power of the anion to co-ordinate with mercury. We have found specific catalysis by iodide, bromide, chloride, and acetate ions, diminishing in that order; but none by acetic acid molecules, and none, as was shown in Part IV,[1] by nitrate ions.

Since two new types of transition state were clearly involved in these catalysed reactions, we had to contemplate two new and independent tasks of establishing the stereochemical course of the substitution under catalytic conditions, known as to kinetic form. Therefore, in order to build up the necessary kinetic background, we changed, in

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* This last conclusion may need a further word. All pre-equilibrium complexings must be either slight, or almost complete, in order to account for the linearities. If the second complexing were nearly complete, a second break would appear where the concentration of lithium bromide equals the sum of those of the mercuric and methylmercuric bromide—exactly as the near-completeness of the first complexing leads to the break we find. Therefore, our curve shows that, whilst the first complexing is nearly complete, the second is only slight.

these further kinetic studies, from methyl to s-butyl systems, such as could afterwards be examined in optically active form.

The following mercury-exchange reactions have been studied kinetically, by the transfer of radioactivity, due to ^{203}Hg, from the mercuric to the s-butylmercuric salt:

$$\left.\begin{array}{l} \mathrm{Bu^sHgI} + \overset{*}{\mathrm{Hg}}\mathrm{I_2} \overset{\text{KI}}{\rightleftharpoons} \mathrm{Bu^s}\overset{*}{\mathrm{Hg}}\mathrm{I} + \mathrm{HgI_2} \\ \mathrm{Bu^sHgBr} + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \overset{\text{LiBr}}{\rightleftharpoons} \mathrm{Bu^s}\overset{*}{\mathrm{Hg}}\mathrm{Br} + \mathrm{HgBr_2} \\ \mathrm{Bu^sHgCl} + \overset{*}{\mathrm{Hg}}\mathrm{Cl_2} \overset{\text{LiCl}}{\rightleftharpoons} \mathrm{Bu^s}\overset{*}{\mathrm{Hg}}\mathrm{Cl} + \mathrm{HgCl_2} \end{array}\right\} \text{acetone at } 35^\circ$$

$$\left.\begin{array}{l} \mathrm{Bu^sHg{\cdot}OAc} + \overset{*}{\mathrm{Hg}}\mathrm{(OAc)_2} \overset{\text{LiOAc}}{\rightleftharpoons} \mathrm{Bu^s}\overset{*}{\mathrm{Hg}}\mathrm{{\cdot}OAc} + \mathrm{Hg(OAc)_2} \\ \mathrm{Bu^sHg{\cdot}OAc} + \overset{*}{\mathrm{Hg}}\mathrm{(OAc)_2} \overset{\text{HOAc}}{\rightleftharpoons} \mathrm{Bu^s}\overset{*}{\mathrm{Hg}}\mathrm{{\cdot}OAc} + \mathrm{Hg(OAc)_2} \end{array}\right\} \text{ethanol at } 60^\circ$$

The various rate-constants for these reactions are collected in Table 2.

TABLE 2. *First-order rate-constants of label-transfer (k_1^{Hg} in sec.$^{-1}$) rates of exchange (k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$) and second-order rate-constants of one-alkyl substitution ($k_{2c}^{(1)}$ in mole^{-1} l. sec.$^{-1}$) by mercuric salts (concentration a) in s-butylmercuric salts (concentration b) with added alkali-metal salts or acetic acid (concentration c).*

[The radioactive label was initially in the mercuric salt. Concentrations were set at the reaction temperatures, and hence no corrections for thermal expansion are necessary. As to $k_{2c}^{(1)}$ (calc.) see Section 5.]

Run	*a* (M)	*b* (M)	*c* (M)	$10^6k_1^{\mathrm{Hg}}$	$10^7k_0^{\mathrm{Hg}}$	$10^5k_{2c}^{(1)}$ (obs.)	$10^5k_{2c}^{(1)}$ (calc.)
	s-Butylmercuric iodide, mercuric iodide, and potassium iodide, in acetone at 35·0°						
205	0·050	0·150	0·000	0·00	0·00	0·00	—
211	0·045	0·135	0·0056	1·42	0·48	0·79	0·62
212	0·045	0·135	0·0224	4·14	1·40	2·30	2·49
210	0·041	0·163	0·0120	2·49	0·82	1·22	1·46
207	0·053	0·163	0·056	18·6	7·4	8·6	6·2
209	0·053	0·163	0·112	56·9	22·7	26·3	28·6
208	0·106	0·163	0·112	16·4	10·6	6·1	7·4
	s-Butylmercuric bromide, mercuric bromide, and lithium bromide, in acetone at 35·0°						
201	0·300	0·300	0·000	0·00	0·00	0·00	—
214	0·022	0·201	0·244	5·00	0·99	2·25	2·00
213	0·028	0·196	0·275	4·48	1·00	2·00	2·13
	s-Butylmercuric chloride, mercuric chloride, and lithium chloride, in acetone at 35·0°						
200	0·150	0·350	0·000	0·00	0·00	0·00	—
215	0·090	0·204	0·468	0·94	0·58	0·32	0·30
	s-Butylmercuric acetate, mercuric acetate, and lithium acetate, in ethanol at 59·8°						
102	0·090	0·127	0·000	37·3	36·5	32	—
109	0·101	0·112	0·0465	308	164	145	124
114	0·105	0·110	0·0968	455	244	211	216
115	0·105	0·102	0·148	450	250	217	232
	s-Butylmercuric acetate, mercuric acetate, and acetic acid, in ethanol at 59·8°						
102	0·090	0·127	0·000	37·3	36·5	32	—
105	0·101	0·137	0·113	83·3	47·0	35	—
106	0·123	0·140	0·349	86·2	56·5	33	—

The strongest catalysis here is by the alkali-metal iodide on the exchange of s-butylmercuric and mercuric iodides. The figures are not suitable for graphical representation, but an analysis of them (Section 5) shows that we have again both one-anion and two-anion catalysis. And again, the effectiveness of the two-anion catalysis is reduced when, with the concentration of alkali-metal salt in excess over that of the mercuric salt, the latter concentration is increased. The catalysis generally falls off along the series, iodides, bromides, chlorides, acetates. In the exchange of s-butylmercuric and mercuric acetates, as affected by the alkali-metal acetate, the one-anion catalysis, though undoubtedly specific, is relatively mild, and the two-alkyl catalysis is inappreciable, the rates rising to a limit as the concentration of catalyst equals and surpasses that of the mercuric salt. In the same exchange, in the absence of an alkali-metal salt, but in the presence of acetic acid, no catalysis is apparent.

(4) *Steric Course of the One- and Two-anion-catalysed One-alkyl Substitutions.*—One-alkyl catalysis was stereochemically investigated in the example of the exchange reaction of optically active s-butylmercuric iodide with mercuric iodide in acetone, in the presence of a concentration of potassium iodide equal to that of the mercuric iodide. Practically the whole of the reaction is then of the one-anion-catalysed type. As shown in Table 3, the s-butylmercuric iodide recovered after two half-lives had its optical activity completely unchanged.

Two-alkyl catalysis was similarly examined in the exchange reaction of optically active s-butylmercuric bromide with mercuric bromide in acetone, in the presence of lithium bromide in an excess of the order of 10-fold over the mercuric bromide. Nearly the whole of the reaction now proceeds by the two-anion-catalysed mechanism. The same stereochemical result was obtained; and it was used preparatively in order to produce the optically active and radioactive s-butylmercuric bromide required for use in the work of Part III.[2] Some of these runs were followed for very long periods, the longest that of the second run recorded in Table 3

TABLE 3. *Initial and final optical rotations of s-butylmercuric halides in exchange reactions with mercuric halides under catalysis by alkali-metal halides in acetone at* 35·0°.

(The concentrations *a*, *b*, and *c*, have the significance given in the heading of Table 2. Specific rotations $[\alpha]_D^{20}$ are for c = 5, in acetone; X = I or Br.)

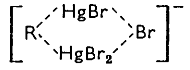
Run	*a* (M)	*b* (M)	*c* (M)	½-lives followed	$[\alpha]_D^{20}$ of Bu^sHgX initial	final
One-anion catalysis: $Bu^sI + HgI_2 + KI$						
220	0·1	0·1	0·1	2	+3·4°	+3·4°
Two-anion catalysis: $Bu^sBr + HgBr_2 + LiBr$						
230	0·2	0·2	1·7	200	+4·5°	+4·5°

It follows from these polarimetric results that both the one-anion and the two-anion mechanisms of one-alkyl mercury-exchange preserve stereochemical configuration completely.

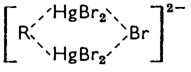
(5) *Mechanisms of the Anion-catalysed One-alkyl Substitutions.*—Let us first consider the broad picture of known specific salt effects on electrophilic mercury-for-mercury substitutions, as disclosed in Parts II [3] and III [2] and in this paper, using the behaviour of lithium bromide as example. We seek to understand why the two-alkyl substitution of mercuric bromide in a dialkylmercury is so strongly retarded by lithium bromide that an amount of it equivalent to that of the mercuric bromide practically puts the latter out of action; whereas in the three-alkyl substitution of an alkylmercuric bromide in a dialkylmercury, lithium bromide exerts at most only a small specific retardation—small enough to be difficult to disentangle from the general salt effect; and yet, in the one-alkyl substitutions of mercuric bromide in alkylmercuric bromides, we find lithium bromide conferring the great accelerations here described. We think the explanation must be that a bromide ion can co-ordinate strongly with mercuric bromide, weakly with an alkylmercuric bromide, and not at all with a dialkylmercury. Then, in the two-alkyl substitution, the bromide ion will combine strongly with the initial state to form the anion $HgBr_3^-$, but only weakly with the transition state, in which the mercury of the original

mercuric salt has in part become an alkylmercuric mercury atom: hence the strong retardation. In the three-alkyl substitution, the bromide ion can combine only weakly with the initial state, and still more weakly or not at all with the transition state; hence the quite trivial retardation. In the one-alkyl substitution, the bromide ion can combine strongly with the initial state, again to form $HgBr_3^-$, but more strongly with the transition state, in which it can bridge the mercury atoms, gaining stability by partial substitution of very stable $HgBr_2$-molecule bonding for much less stable $HgBr_3^-$-ion bonding.[5] The bromide ion not only can, but *must* bridge, because it enters, as $HgBr_3^-$, with the lower Hg of formula (I), and leaves, as $HgBr_2$, with the upper one; and hence it must be on its way from one mercury to the other in the transition state. We thus describe what our kinetics distinguish as one-anion catalysis: it implies the closed transition state (I), and exemplifies the internal mechanism of electrophilic substitution, S_Ei, which was anticipated in Part I,[4] and is now found for the first time.

(I)



Transition state for one-anion catalysis



(II)

Transition state for two-anion catalysis

One bromide ion having thus been taken into the reacting system, a second bromide ion could, and, as our kinetics show, does, in part, intervene. This second bromide ion could combine in the initial state to form either $HgBr_4^{2-}$, or $RHgBr_2^-$, or both, and with transition state (I) to form transition state (II), which might thus express the course of two-anion catalysis. It would be difficult to predict whether this second bromide ion should be bound in the initial or in the transition state the more strongly. Thus, in solution, as we point out below, $HgBr_2$ and Br^- combine to form $HgBr_3^-$ considerably more exothermally than $HgBr_3^-$ and Br^- combine to form $HgBr_4^{2-}$. But how uptake of the last bromide ion to produce one free $HgBr_4^{2-}$ ion in the initial state compares thermodynamically with its uptake to give two partly freed $HgBr_3^-$ ions in transition state (II), cannot be foreseen. If there were nothing to choose, and if also the alternative site in $RHgBr_2^-$ for the last-added bromide ion in the initial state were so unfavourable that it could be disregarded, then our one-anion and two-anion catalyses would have been just equally strong, and the latter, despite its presence and importance, could not have been distinguished by the simple method illustrated in the Figure. But the two-anion catalysis is somewhat the stronger, and is detected by this character. We conclude that the last-added bromide ion is actually combined somewhat more strongly in transition state (II) than in the corresponding initial state.* Transition state (II) thus represents the observed two-cation catalysis, which provides a second example of the expected mechanism S_Ei.

Though they are explained above with reference to catalysis by bromide ion, we regard these mechanisms as applicable to all the one-anion and two-anion catalyses described in this paper. In the case of acetate ion, only one-anion catalysis appears. It does not logically follow, but it is possible that this anion uses both its oxygen atoms to close the cyclic transition state.

One could gain the impression from some books that, among complex mercury halides, the doubly charged ones, HgX_4^{2-}, are more stable than the singly charged, HgX_3^-, for the same halogen. But this idea may arise in part from a reversal in the solid state of the balance of intrinsic molecular stability, by the greater lattice energies of salts of the doubly

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* Since this was written, we have found a case in which two-anion catalysis is the weaker, so that the two-line curve, corresponding to that shown here, exhibits a decrease of gradient, instead of an increase, at the break.

[4] Charman, Hughes, and Ingold, *J.*, 1959, 2523.

[5] Sillén, *Acta Chem. Scand.*, 1949, **3**, 539; Marcus, *ibid.*, 1957, **11**, 599; Van Panthaleon van Eck, Thesis, Leiden University, 1958.

charged ions. However that may be, our kinetic results, like those of Part II,[3] show clearly that, in dilute solution in ethanol or acetone at least, HgX_3^- is the dominant complex ion.

In an Appendix (p. 1149) we develop a two-constant kinetic equation for one-alkyl substitutions which are concurrently under one-anion and two-anion catalysis. In terms of our already-defined rate-constant of substitution, $k_{2c}^{(1)}$, it is

$$k_{2c}^{(1)}\,(\text{calc.}) = \begin{cases} \kappa_1\, c/a & (c < a) \\ \kappa_1 + \kappa_2(c - a) & (c > a) \end{cases} \quad . \quad . \quad . \quad . \quad . \quad (\text{i})$$

The curve shown, of two linear branches with a break at $c = a$, is a curve of this equation. Now one can see without calculation that the curve could not have that form unless progressively added lithium bromide were at first taken up nearly completely to form $HgBr_3^-$, until an excess of lithium bromide remained, and unless also this excess then entered into combination, *e.g.*, to form $HgBr_4^{2-}$, only to a small equilibrium extent. Consider some alternatives. If the excess of lithium bromide, after $HgBr_3^-$ had been fully formed, were taken up practically completely to form $HgBr_4^{2-}$, then the curve would become horizontal beyond $c = 2a$; *i.e.*, we should see a curve of three linear branches. If $HgBr_4^{2-}$ were so very stable that nearly all the lithium bromide went to form that ion, rather than the ion $HgBr_3^-$, from the beginning, then no break should occur at $c = a$, but the curve should turn horizontally at $c = 2a$; *i.e.*, we should have a two-branch curve with a break of the wrong form in the wrong place. In situations intermediate between the three limiting ones already considered, the linearities would be lost. Evidently, the bromide ion added as lithium bromide is stored nearly to the stoicheiometrically possible extent as $HgBr_3^-$ throughout our experimental range. This interpretation agrees with and includes, the assumption which had to be made in order to account for the kinetics of the anticatalysis by lithium bromide of the two-alkyl substitution treated in Part II.*

Collateral evidence on the relative stabilities of the singly and doubly charged complex halides of mercury relates largely to solvent water, wherein solvation heat, analogously to the lattice energy, may favour the doubly charged species. However, even here the singly charged ions seem to predominate. Garrett[6] could interpret the solubility of mercuric bromide in aqueous potassium bromide with the aid of a good equilibrium constant for complex formation, only on the basis that the complex was $HgBr_3^-$, though it is allowed that a little $HgBr_4^{2-}$ may be formed when both Br^- and $HgBr_3^-$ are in high concentration. Delwaulle and her collaborators showed[7] that the one-band Raman spectrum of $HgBr_2$ is almost completely replaced by a different spectrum, one of two bands, as would be expected for $HgBr_3^-$, assuming analogy with BF_3, when, in aqueous or ethanolic solution, one equivalent of an alkali bromide is added; and that, on the addition of a second equivalent, no similarly distinct new spectrum appears, but the two bands merely undergo shifts, such as might arise from the electrostatic effect of ambient ions, rather than from the incursion of a new spectral source in $HgBr_4^{2-}$, which should produce a four-band spectrum.† It has been shown,[5] both theoretically and practically, that the enthalpy and free-energy of binding of the last bromide ion in $HgBr_4^{2-}$ in water is considerably smaller than that of the last in $HgBr_3^-$, and is insufficient to hold $HgBr_4^{2-}$ together to any great extent except in very concentrated solutions.

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* One of two criteria, used in Part II[3] to distinguish mechanisms S_E2 and S_Ei in two-alkyl exchange, was that, with bromides as reactants, complexing with lithium bromide theoretically should decrease an S_E2 rate (as it does the observed rate), but " might well " (as we put it) increase an S_Ei rate. We can now eliminate the slight reserve from this last statement, because we know observationally now, as we did not then, that such complexing does indeed increase S_Ei rates in systems suited to the formation of cyclic transition states.

† This interpretation is slightly different from that of the authors, who seem not to have considered the selection rules.

[6] Garrett, *J. Amer. Chem. Soc.*, 1939, **61**, 2744.

[7] Delwaulle, François, and Wiemann, *Compt. rend.*, 1938, **106**, 1100.

To return to equation (i): we can choose constants, κ_1 and κ_2, as in Table 4, and from them deduce the values of $k_{2c}^{(1)}$ (calc.) which are in the last columns of Tables 1 and 2. Comparison with $k_{2c}^{(1)}$ (obs.) reveals general agreement, but also some systematic deviations (Table 1, near the bottom). These are just such as would be expected if two of the assumptions, which we had to make (Appendix) in order to reduce the number of disposable constants to two, were not quite correct; in particular, if $HgBr_3^-$ were not formed quite stoicheiometrically, and if the formation of $RHgBr_2^-$ were not quite inappreciable. We have already noted other indications that both these things are true. Of course, we could make the relevant allowances theoretically, and so obtain a nearly perfect fit between theory and experiment; but this would entail the introduction of two more disposable constants.

The catalytic constants, κ_1 and κ_2, depend on reactant-structure, solvent, and temperature jointly; but the ratio κ_2/κ_1 should be more simply related to the affinity of the catalysing anion for mercury. The order of affinity thus indicated is I > Br > OAc. Van Panthaleon van Eck's binding energies of halide ions with mercury [5] give the order I > Br > Cl.

The two mechanisms of mercury-for-mercury substitution, epitomised in the transition-state formulæ (I) and (II), obviously require retention of stereochemical configuration.

TABLE 4. *Catalytic constants for one- and two-anion-catalysis* (κ_1 *in mole*$^{-1}$ *l. sec.*$^{-1}$ *and* κ_2 *in mole*$^{-2}$ *l.*^{2} *sec.*$^{-1}$) *by the anion* X *in one-alkyl substitutions by* HgX_2 *in* RHgX

Solvent	Temp.	R	X	$10^5\kappa_1$	$10^5\kappa_2$	κ_2/κ_1
Acetone	35·0°	Bu^s	I	5	400	80
,, ...	,,	,,	Br	Small	9	—
,, ...	,,	,,	Cl	Small	0·8	—
Ethanol	59·8	Me	Br	35	500	14
,, ...	,,	Bu^s	OAc	200	Small	~0

As is shown in Section 4, configuration is fully retained in both the one-anion- and the two-anion-catalysed substitutions.

Our general conclusion is that the mercury exchanges of mercuric salts with alkylmercuric salts, when specifically catalysed by anions which can co-ordinate with the mercury atoms, use forms of the internal mechanism of electrophilic substitution, S_Ei, contemplated in Part I.[4]

EXPERIMENTAL

Materials.—The sources of the substances here used have been noted in Parts I—IV.[1-4] with the exception of s-butylmercuric chloride and iodide. The chloride, which was precipitated at first as an oil on addition of aqueous hydrochloric acid to a solution in acetone of s-butylmercuric hydroxide,[4] had m. p. 29° when crystallised from ethanol. The iodide, which separated as a solid when aqueous potassium iodide was added to the acetone solution of hydroxide, had m. p. 52° after crystallisation from ethanol; it became yellow on storage in ordinary conditions, and was therefore kept at 0° in the dark, and was crystallised from pentane just before use.

Kinetics.—The methods of starting and stopping runs, of separating products from timed samples for radiometric or polarimetric examination, and the methods of these examinations, have been described in Part IV.[1] The conditions of the runs, and the rate-constants obtained, are given in Tables 1 and 2 above. We do not here record a specimen run, as any of our runs would be closely similar to one of those recorded as specimens in Part IV.[1]

APPENDIX

A full mass-law derivation of the rate equation for anion-catalysed one-alkyl mercury exchange would involve four equilibrium constants of complex formation (stability constants), and five rate-constants for individual substitutions of the complexes—a ridiculous number of disposable constants. We have therefore assumed the equilibrium constants of complex formation to be either very large or very small, as indicated by the reversed-arrow signs below.

This has the effect, not only of simplifying the algebra, but also of bunching the nine constants into two sets, with some constants belonging to both sets, which we can then replace by two omnibus constants, so reaching a formula which has some meaning in application to observational data.

The catalytic anion being X^-, the four complexing equilibria are taken to be strongly unbalanced, with equilibrium constants as follows:

$$\mathrm{X^- + HgX_2 \overset{K_1}{\rightleftharpoons} HgX_3^-}$$
$$\mathrm{X^- + HgX_3^- \overset{K_2}{\rightleftharpoons} HgX_4^{2-}}$$
$$\mathrm{X^- + RHgX \overset{K_3}{\rightleftharpoons} RHgX_2^-}$$
$$\mathrm{X^- + RHgX_2^- \overset{K_4}{\rightleftharpoons} RHgX_3^{2-}}$$

These equilibria lead to equilibria with the following constants, between five possible pairs of reactants for substitution:

$$\underbrace{\mathrm{RHgX + HgX_3^-}}_{\mathrm{A}} \underset{K_3/K_1}{\rightleftharpoons} \underbrace{\mathrm{RHgX_2^- + HgX_2}}_{\mathrm{B}}$$

$$\underbrace{\mathrm{RHgX + HgX_4^{2-}}}_{\mathrm{C}} \underset{K_3/K_2}{\rightleftharpoons} \underbrace{\mathrm{RHgX_2^- + HgX_3^-}}_{\mathrm{D}} \underset{K_4/K_1}{\rightleftharpoons} \underbrace{\mathrm{RHgX_3^{2-} + HgX_2}}_{\mathrm{E}}$$

For brevity, we designate the reactant pairs A—E, and define the respectively relevant second-order rate-constants of substitution as follows:

$$\text{Contributions to one-anion catalysis:}\left\{\begin{matrix} \mathrm{A} \text{—} k_{\mathrm{A}} \rightarrow \\ \mathrm{B} \text{—} k_{\mathrm{B}} \rightarrow \end{matrix}\right\}\text{Products}$$

$$\text{Contributions to two-anion catalysis:}\left\{\begin{matrix} \mathrm{C} \text{—} k_{\mathrm{C}} \rightarrow \\ \mathrm{D} \text{—} k_{\mathrm{D}} \rightarrow \\ \mathrm{E} \text{—} k_{\mathrm{E}} \rightarrow \end{matrix}\right\}\text{Products}$$

Let a, b, and c be the stoicheiometric (*i.e.*, the introduced) concentrations of HgX_2, RHgX, and MX respectively. Let $\bar{a}$, $\bar{b}$, and $\bar{c}$ be the concentrations, respectively, in which these substances survive when all the equilibria formulated above have been established. And let $\bar{d}$, $\bar{e}$, $\bar{f}$, and $\bar{g}$ be the concentrations of the complexes, HgX_3^-, HgX_4^{2-}, $RHgX_2^-$, and $RHgX_3^{2-}$, respectively, when all the equilibria are established.

Case 1. Consider first the case in which MX is in deficit: $c < a$. Then, because of our assumptions concerning the equilibria, $\bar{b} = b$ and $\bar{d} = c$. Hence the rate of the reaction of A will be $k_{\mathrm{A}}\overline{bd} = k_{\mathrm{A}}bc$. Because of the equilibrium between A and B, the rate of the reaction of B will be $k_{\mathrm{B}}(K_3/K_1)bc$. The sum of these rates is that of one-anion catalysis. It is easily seen that the rates of the reactions of C, D, and E, which compose two-anion catalysis, will be negligible in comparison with their respective rates in the case, next to be considered, in which two-anion catalysis becomes comparable in magnitude with one-anion catalysis. Since when we reduce c, two-anion catalysis fades out at first, we can safely assume that it makes no effective contribution to substitution rate in the present case. Hence the total rate, which is simply the exchange rate, k_0^{Hg}, is given by

$$k_0^{\mathrm{Hg}} = \left(k_{\mathrm{A}} + k_{\mathrm{B}} \, . \, \frac{K_3}{K_1}\right) bc = \kappa_1 \, bc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(ii)}$$

where κ_1 is our first omnibus constant, and is defined by this equation.

Case 2. Consider now the situation in which MX is in excess: $c > a$. Then, as before, $\bar{b} = b$; but now $\bar{c} = c - a$, and $\bar{d} = a$. Also $\bar{e} = K_2\overline{cd} = K_2a(c - a)$; and $\bar{f} = K_3\overline{bc} = K_3b(c - a)$. The rate of the reaction of A will now be $k_{\mathrm{A}}\overline{bd} = k_{\mathrm{A}}ab$, and, as before, that of the reaction of B will be $(k_{\mathrm{B}}/k_{\mathrm{A}})(K_3/K_1)$ times this. Hence, the contribution of one-anion catalysis to the rate will be $\{k_{\mathrm{A}} + k_{\mathrm{B}}(K_3/K_1)\}ab = \kappa_1ab$ by (ii). The rate of the reaction of C will be $k_{\mathrm{C}}\overline{be} = k_{\mathrm{C}}K_2\,ab(c - a)$; the rate of the reaction of D will be $k_{\mathrm{D}}\overline{df} = k_{\mathrm{D}}K_3ab(c - a)$; and the rate of the reaction of E will be $(k_E/k_D)(K_4/K_1)$ times this. These three rates compose the contribution of two-anion catalysis to the total rate, which will be

$$k_0^{Hg} = \left\{\kappa_1 + \left(k_C K_2 + k_D K_3 + k_E \frac{K_3 K_4}{K_1}\right)(c - a)\right\} ab = \{\kappa_1 + \kappa_2(c - a)\} ab \quad . \quad \text{(iii)}$$

where κ_2 is our second omnibus constant, and is defined by this equation.

If $c \approx a$, so that $(c - a)$ becomes of the order of the error in our setting of the equilibrium (barred) concentrations—errors arising from the circumstance that the equilibrium constants, taken as large or small, are in reality neither infinite nor infinitesimal—then equations (ii) and (iii) will not hold. But the range of c so affected may well be small enough, or else the disturbances many be sufficiently self-compensatory, to allow them to pass unnoticed in experiments at spaced-out c values. Supposing this to be so, we can combine equations (ii) and (iii) at $c = a$, at which they give the same rate, $\kappa_1 ab = \kappa_1 bc$. Then, using the definition of $k_2^{(1)}$ given in Section 2 of Part IV,[1] *viz.*, $k_0^{Hg} = k_2^{(1)} ab$, we arrive at equation (i), already set down in Section 5 of this paper.

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