

227. *Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part IV.* Kinetics, Stereochemistry, and Mechanism of the Uncatalysed One-alkyl Mercury-exchange Reaction.*

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The reactions of mercury exchange of methylmercuric and/or *s*-butylmercuric bromide, iodide, acetate, and nitrate, with mercuric salts having corresponding anions, exemplify the formerly expected, but now newly recognised, one-alkyl form of electrophilic mercury-for-mercury substitution, which here proceeds in ethanol by mechanism S_E2 with full retention of configuration. The evidence is as follows. It is shown by a radiometric study of the kinetics of the mercury exchanges, that they go in a single bimolecular step. By using optically active *s*-butylmercuric acetate, it is shown in a correlated polarimetric study that the substitution produces no loss of optical activity. By increasing the ionicity of the salts along the anion-series mentioned, and noting the associated large increase in rate, it is shown that reaction is not assisted by combination between the anion of the substituting agent and the mercury atom being expelled, *i.e.*, that we have an open, rather than a closed, transition state. Confirmatively, substantial positive salt-effects and polar co-solvent-effects are observed, which show that the transition states are considerably more polar than the initial states.

All the three expected forms of aliphatic mercury exchange have now been observed and their mechanisms demonstrated.

(1) *Previous Work.*—The one-alkyl electrophilic mercury-for-mercury substitution can be demonstrated only with the aid of isotopically labelled mercury, as by radioactive ^{203}Hg , in an isotopic exchange reaction, such as the following, where the asterisk signifies the label:



This isotopic exchange was first described by Nefedov and Sintova.^{1,2} They did not recognise it as a new form of substitution. Reutov generalised it to other alkyl groups including cycloalkyl and arylalkyl groups.^{3,4,5} He recognised it as depending on electrophilic substitution. With Knoll and Wu Yan-Tsei, he studied its stereochemistry, both with geometrical isomers in the cyclohexane series and with menthyl derivatives having centres of asymmetry, besides the metal-bearing one, in optically active form.³ These authors concluded that configuration is retained.

Nefedov and Sintova regarded their reaction, not as the individual process formulated

* Part III, preceding paper.

¹ Nefedov and Sintova, "Collected Works on Radiochemistry," Leningrad University Press, 1955, p. 113.

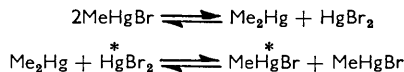
² Nefedov, Sintova, and Frolov, *Zhur. fiz. Khim.*, 1956, **30**, 2356.

³ Reutov, Knoll, and Wu Yan-Tsei, *Doklady Akad. Nauk S.S.S.R.*, 1958, **120**, 1052.

⁴ Reutov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1958, 684.

⁵ Reutov, *Angew. Chem.*, 1960, **72**, 198.

above, but as the overall result of two successive substitutions of the long-familiar two-alkyl type:



Their reasons for this view are not apparent. Their rate figures, though neither extensive nor accurate enough to justify a positive conclusion, tend more against their interpretation than in favour of it. However, the interpretation seems to have been accepted, at least until recently, when Reutov remarked⁵ that some unpublished work had convinced him that it could not be generally valid.*

(2) *Kinetic Form of the Uncatalysed One-alkyl Substitution.*—This history exposes the first essential question, *viz.*, that of whether the exchange is indeed the independent one-alkyl substitution, which was anticipated as a realisable electrophilic substitution in Part I⁶ [cf. equations (a) and (1) of the preceding paper], when it would be, not observationally new, but a newly identified reaction, demanding an investigation of its mechanism, or whether it is a composition of steps of the well-known two-alkyl electrophilic substitution [cf. equations (c) and (2) of the preceding paper], in which case there would be nothing more to do, since the mechanism of that reaction for simple alkyl groups has been established (Part II⁷).

This question cannot be answered, like the similar one concerning three-alkyl substitution, dealt with in Part III,⁸ by double-labelling; but it can by a suitable study of kinetic form. The formulæ of the Appendix of Part III⁸ apply with little change. If *a* is the concentration of the substituting agent, here the mercuric salt, and *b* is that of the compound substituted, *viz.*, the alkylmercuric salt, then, independently of the mechanism of exchange, the observational first-order rate-constant of label-transfer, k_1^{Hg} , will give an exchange-rate, $k_0^{\text{Hg}} = k_1^{\text{Hg}}ab/(a + b)$. And then, if exchange depends on a succession of two-alkyl substitutions, a second-order constant $k_2^{(2)} = k_0^{\text{Hg}}/b^2$, will be invariant with changing *a* and *b*, apart from any medium effects. But if the exchange is manifesting a single one-alkyl substitution, then the only second-order constant which could possess this property is $k_2^{(1)} = k_0^{\text{Hg}}/ab$.

It will, however, possess it only if the one-alkyl substitution proceeds in a single step of molecularity two, as in either mechanism $S_{\text{E}2}$ or mechanism $S_{\text{E}i}$ (Part I⁶). But the single substitution might involve two distinct reactions, *e.g.*, a slow alkyl ionisation, followed by a rapid entry of the substituting agent, as in mechanism $S_{\text{E}1}$ (Part I⁶). In that case, no second-order constant will be invariant with changing *a* and *b*, but the first-order constant, $k_1^{(1)} = k_0^{\text{Hg}}/b$, will be so, apart from medium effects. Thus, if the one-alkyl substitution is indeed under observation, a determination of its kinetic form will not only identify it as such, but will also make a significant contribution to the establishment of its mechanism.

We first applied this procedure in Nefedov and Sintova's example,† that of mercury exchange between methylmercuric bromide and mercuric bromide in ethanol at 100°, with our label of the radioactivity of ²⁰³Hg initially in the mercuric bromide. The rate-constants of label-transfer and exchange, and the various rate-constants of substitution, calculated therefrom according to mechanism, are in the uppermost portion of Table 1.

The constants $k_2^{(2)}$ and $k_1^{(1)}$ evidently vary systematically with the concentrations of one or both reactants, and only the constants $k_2^{(1)}$ exhibit no more scatter than is of the

* We made an equivalent statement in Part I,⁶ on the basis of work preliminary to that now reported.

† These authors' exchange rates² are more than twice as large as ours in like conditions. We do not know the cause of the discrepancy, but it might arise from the circumstance that they separated methylmercuric bromide from mercuric bromide in timed reaction samples by steam-distilling the former, a method which, in our hands, led to exchange during separation.

⁶ Charman, Hughes, and Ingold, *J.*, 1959, 2523.

⁷ Charman, Hughes, and Ingold, *J.*, 1959, 2530.

⁸ Charman, Hughes, Ingold, and Thorpe, preceding paper.

order of the observational error. Any medium effects are within the range of casual variation of the rate constants. This result both identifies the exchange with one-alkyl substitution, and shows that this substitution proceeds in a single step.

The second portion of Table I shows the effect of temperature. We did not prove the applicability of the Arrhenius equation, but the substitution constants $k_2^{(1)}$ at 60° and 100° are given by the equation $k_2^{(1)} = 10^{7.70} \exp(-19,800/RT)$, which we shall use below for making an approximate extrapolation with respect to temperature.

The last section of Table I shows that the addition of 10% of water to the solvent ethanol accelerates the reaction by a factor of 1.83 at 100°. We take this to indicate that the reaction goes faster in more polar solvents generally, implying a polar transition state, for which we shall adduce further evidence below.

(3) *Kinetic Form: Generalisation to Other Anions, and to Another Alkyl Group.*—We report in this Section a series of analogous kinetic investigations, all with ethanol as

TABLE I. *First-order rate-constants (k_1^{Hg} in sec.⁻¹) of transfer of radioactivity, rates of mercury exchange (k_0^{Hg} in mole l.⁻¹ sec.⁻¹) and first-order ($k_1^{(1)}$ in sec.⁻¹) and second-order ($k_2^{(2)}$ and $k_2^{(1)}$ in mole⁻¹ l. sec.⁻¹) rate-constants for substitution by mercuric bromide (concentration a) in methylmercuric bromide (concentration b).**

Run	a (M)	b (M)	$10^6 k_1^{\text{Hg}}$	$10^7 k_0^{\text{Hg}}$	$10^5 k_2^{(2)}$	$10^6 k_1^{(1)}$	$10^5 k_2^{(1)}$
<i>In ethanol at 100.2°.</i>							
14	0.100	0.100	25.6	12.8	12.8	12.8	12.8
50A	0.091	0.091	19.7	8.9	10.8	9.8	10.8
50B	0.163	0.100	35.0	21.7	21.7	21.7	13.3
30	0.181	0.091	35.9	21.6	26.2	23.8	13.2
13	0.091	0.181	34.8	21.0	6.4	11.6	12.8
29	0.272	0.050	44.7	18.9	75.6	37.8	13.9
19	0.290	0.096	49.4	35.6	38.7	37.1	12.8
129	0.091	0.190	34.3	21.1	5.8	11.1	12.2
57	0.091	0.243	37.1	24.5	4.2	10.1	11.1
121	0.100	0.272	49.5	36.2	4.9	13.3	13.3
122	0.254	0.226	61.4	73.5	14.4	32.5	12.8
128	0.391	0.231	86.5	126	23.5	54.4	13.9
123	0.378	0.281	84.4	136	17.2	48.4	12.8
							Mean: 12.8
<i>In ethanol at 59.8°.</i>							
63	0.095	0.095	0.87	0.42	0.46	0.44	0.46
89	0.095	0.095	0.97	0.46	0.51	0.48	0.51
90	0.173	0.096	1.43	0.88	0.96	0.92	0.53
							Mean: 0.50
<i>In ethanol containing " 10% " of water † at 100.2°.</i>							
130	0.091	0.091	43.6	19.8	—	—	23.9
131	0.094	0.091	41.8	19.3	—	—	22.6
							Mean: 23.3

* Concs., and, where necessary, rate-constants are corrected for thermal expansion of the solvent.

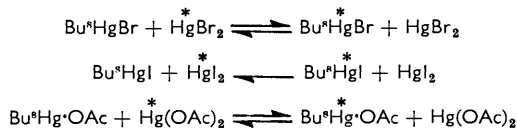
† The mixed solvent was prepared by making 10.0 ml. of water up to 100.0 ml. with 91.6 ml. of ethanol at 20°, there being a contraction of 1.6 ml. on mixing.

solvent. Three of them relate to methylmercuric-mercuric exchange reactions involving anions other than bromide, *viz.*, the exchanges;



where X = I, OAc, and NO₃ severally. The motive here was to set up a distinction, by comparison of the absolute rates of mercury exchanges with different anions, between the two second-order mechanisms of one-alkyl electrophilic substitution, S_E2 and S_Ei, as was done for the two-alkyl⁷ and three-alkyl substitutions.⁸ It was necessary to know, for any reactions thus to be compared as to rate, that their kinetic forms were the same.

We also report here on the kinetic effect of changing the alkyl groups from methyl to *s*-butyl. The motive now was to prepare the way for a correlated stereochemical investigation with an optically active *s*-butylmercuric salt. Charman had made⁹ a preliminary kinetic examination of the three exchange reactions,



and concluded that the first two of them are appropriate neither for a more extended kinetic study, nor, therefore, for correlated stereochemical work, because side-reactions, leading to insoluble (probably mercurous or other polymeric) salts, set in too early. On the other hand, the acetate reaction gave him no serious trouble on account of side-reactions, though these do occur in protracted experiments; and it is on the basis of that knowledge that we have developed a correlated kinetic and stereochemical study of this substitution. In this Section, we report the determination of its kinetic form.

The rate-constants on which all these additional determinations of kinetic form depend are collected in Table 2. They are all for reactions in ethanol, except that the methyl-group-nitrate-ion reaction was conducted in ethanol containing a small amount of nitric acid (and a kinetically scarcely significant amount of water) in order to secure complete solubility and stability of the reactants at the temperature and concentrations used. The reactions were not all studied at the same temperature, because some of them go inconveniently fast at one or both of the temperatures, 100° and 60°, used in the work reported in Section 2 on the methyl-group-bromide-ion reaction. The temperatures, however, are immaterial to the determination of kinetic form. And, since the temperature-coefficient of the rate in ethanol of the methyl-group-bromide-ion reaction is known (Section 2), the temperature differences offer no obstacle to the intended comparison of the widely separated rates we find. As before, our label of radioactivity was initially in the mercuric salt.

In all these cases, the second-order two-alkyl-substitution rate-constant, $k_2^{(2)}$, and also the first-order one-alkyl constant, $k_1^{(1)}$, vary systematically with reactant concentration, and only the second-order one-alkyl constant, $k_2^{(1)}$, remains invariant with changing concentrations to within the observational error. Therefore, all these reactions, including the one of which we have studied the stereochemistry, must be one-alkyl substitutions going in a single step of unit molecularity in each reactant. Thus, as far as this test shows, they can fairly be considered together with respect to mechanism.

(4) *Salt Effects on the One-alkyl Substitution.*—We have to start this Section with a pre-view of some conclusions, in order to explain its scope, and, incidentally, why the word “uncatalysed” occurs in the title of this paper, and in those of some of its Sections. Our finding is that, phenomenologically, the one-alkyl mercury-exchange displays two kinetic salt effects, both positive, but of very different magnitudes. One is small enough to be understood as a normal (or primary) salt-effect, essentially a form of medium effect. The other is specific to certain anions, such as halide ions, which co-ordinate with mercuric salts; and this effect is so powerful that it can justly be described as a “catalysis,” thus implying the incursion of a new mechanism. We report here only the “normal” salt effect, the object being to secure some further indication of the mechanism of the “uncatalysed” reaction, with which alone this paper is concerned. The “catalytic” effect, importing, as it does, a completely separate mechanistic problem, is considered in the following paper.

It was reported in Part III⁸ that added lithium nitrate induced weak comparable accelerations, obviously normal salt effects, on the two three-alkyl exchanges thus studied, *viz.*, those of *s*-butylmercuric bromide and nitrate with di-*s*-butylmercury. We therefore

⁹ Charman, Thesis, London University, 1958, p. 82.

examined the kinetic effects of lithium nitrate on two of our one-alkyl exchanges, *viz.*, those of methylmercuric bromide with mercuric bromide and of *s*-butylmercuric acetate

TABLE 2. *First-order rate-constants of label-transfer (k_1^{Hg} in sec.^{-1}), rates of mercury exchange (k_0^{Hg} in $\text{mole l.}^{-1} \text{sec.}^{-1}$) and first-order ($k_1^{(1)}$ in sec.^{-1}) and second-order ($k_2^{(2)}$ and $k_2^{(1)}$ in $\text{mole}^{-1} \text{l. sec.}^{-1}$) rate-constants of substitutions by mercuric salts (concentration *a*) in alkylmercuric salts (concentration *b*).**

Run	<i>a</i> (M)	<i>b</i> (M)	$10^5 k_1^{\text{Hg}}$	$10^6 k_0^{\text{Hg}}$	$10^4 k_2^{(2)}$	$10^5 k_1^{(1)}$	$10^4 k_2^{(1)}$
<i>Methylmercuric bromide and mercuric bromide in ethanol</i>							
Table 1	Various	Various	Various	Various	—	Mean (100·2°)	1·28
"	"	"	"	"	—	Mean (59·8°)	0·050
<i>Methylmercuric iodide and mercuric iodide at 100·2° in ethanol</i>							
49	0·048	0·122	17·5	6·03	4·07	4·97	10·3
56	0·0234	0·122	13·4	2·63	1·76	2·15	9·2
58	0·0211	0·127	15·8	2·87	1·78	2·26	10·7
73	0·073	0·045	12·7	3·25	16·1	7·24	9·9
74	0·073	0·136	21·7	10·3	5·58	7·59	10·4
							Mean: 10·1
<i>Methylmercuric acetate and mercuric acetate at 59·8° in ethanol</i>							
120	0·320	0·058	197	96·5	287	166	52
111	0·0466	0·058	46·0	11·8	35·4	20·5	44
116	0·0762	0·059	70·3	23·4	67·2	39·6	52
119	0·320	0·153	246	255	109	166	52
							Mean: 50
<i>s-Butylmercuric acetate and mercuric acetate at 59·8° in ethanol</i>							
92	0·069	0·104	5·33	2·21	2·09	2·17	3·08
93	0·114	0·120	6·37	3·72	2·58	3·10	2·72
102	0·127	0·090	3·73	3·65	4·50	4·05	3·19
104	0·119	0·247	12·2	9·79	1·60	3·96	3·33
117	0·104	0·325	14·0	11·1	1·05	3·38	3·25
118	0·038	0·341	10·4	3·56	0·306	1·04	2·75
							Mean: 3·05
<i>Methylmercuric nitrate and mercuric nitrate at 0·0° in ethanol containing nitric acid (0·32M) and water (0·8%)</i>							
85	0·125	0·098	35·0	19·2	20·0	19·6	15·7
86	0·117	0·195	53·4	39·0	10·3	10·0	17·1
87	0·223	0·185	71·8	72·7	21·2	39·2	17·6
88	0·140	0·299	75·1	71·6	8·01	23·9	17·1
							Mean: 16·9

* Concentrations and rate-constants are corrected where necessary for thermal volume changes of the solvent.

with mercuric acetate. The radioactive label was, as usual, initially in the mercuric salt. The results are summarised in Table 3.

Lithium nitrate exerts mild accelerating effects on both reactions, a larger one on the methyl-group-bromide-ion reaction than on the *s*-butyl-acetate reaction: but in both, the order of magnitude is the same as that of the effects observed on the two three-alkyl reactions examined. In the bromide reaction, the logarithm of the rate increases linearly with the concentration of added salt. In the acetate reaction, the logarithm rises with a power of concentration which lies below unity but well above one-half. The significance of these results will be considered in Section 6.

(5) *Stereochemical Course of the Uncatalysed One-alkyl Substitution.*—For a study of the stereochemical course of any reaction, one needs clean stoichiometry and well-defined kinetics. The only one of the three examined reactions of *s*-butyl compounds (Section 3)

which was free enough from side-reactions to fulfil this pre-requisite was that of *s*-butylmercuric acetate with mercuric acetate. This reaction goes in ethanol at 59.8°, without measurable disturbance, for at least 2—3 half-lives, say 80% of reaction, which is about as far as the radiometric kinetics could in any case be followed accurately. Nevertheless

TABLE 3. *Effects of added lithium nitrate on the second-order rate-constants of substitution ($k_2^{(1)}$ in mole⁻¹ l. sec.⁻¹) by mercuric salts in alkylmercuric salts in ethanol.**

Run	a (M)	b (M)	[LiNO ₃] (M)	Mean	10 ⁴ k ₂ ⁽¹⁾	Mean
<i>Methylmercuric bromide and mercuric bromide at 100.2°</i>						
Table 1	Various	Various	0.0	0.0	—	1.28
60B	0.091	0.091	0.048	} 0.048	1.83	} 1.92
71	0.091	0.091	0.048		2.00	
72	0.091	0.091	0.091	} 0.096	3.22	} 3.33
25	0.100	0.100	0.100		3.44	
60A	0.091	0.091	0.133	0.133	4.73	4.73
<i>s-Butylmercuric acetate and mercuric acetate at 59.8°</i>						
Table 2	Various	Various	0.0	0.0	—	3.07
113	0.109	0.117	0.115	0.115	4.58	4.58
112	0.105	0.131	0.222	0.222	5.40	5.40
107	0.116	0.143	0.341	0.341	6.00	6.00

* Concentrations and rate-constants are corrected for thermal expansion of the solvent.

there is a very slow decomposition, which, after about 7 half-lives (99% reaction) is shown by the accumulation of an appreciable, and after 40 half-lives, a very substantial, precipitate.

The exchanges with optically active *s*-butylmercuric acetate and mercuric acetate were run with each reactant in concentration 0.1M in ethanol at 59.8°, conditions in which the half-life is 3.1 hours. It was first shown that, with the mercuric acetate omitted, the *s*-butylmercuric acetate could be thus heated in ethanol for a period equal to 40 half-lives of the exchange reaction, without loss of optical activity, and, incidentally, without decomposition leading to a precipitate, such as accompanies the exchange reaction. The observed polarimetric effects accompanying the exchange reaction are noted in Table 4. In all these experiments, the optical activity of the *s*-butylmercuric salt, was measured in the bromide, precipitated from a solution of the acetate with potassium bromide.

TABLE 4. *Polarimetric changes accompanying the mercury-exchange reaction of optically active s-butylmercuric acetate with mercuric acetate in ethanol at 59.8°.*

([*s*-BuHg·OAc] = [Hg(OAc)₂] = 0.100M. Specific rotations, [α]_D²⁰, in acetone, with *c* = 4, are of *s*-butylmercuric bromide, obtained from the acetate, either as used, or as in reaction samples.)

Run	Time (hr.)	½-lives	Reaction (%)	[α] _D ²⁰	Run	Time (hr.)	½-lives	Reaction (%)	[α] _D ²⁰
Initial	0	0	0	-5.7°	186	7.0	2.3	79.7	-5.6°
183	1.0	0.32	19.9	-5.4	184	26.5	8.6	99.7	-5.0
183	3.0	0.97	49.0	-5.6	185	27	8.7	99.7	-5.3
184	3.0	0.97	49.0	-5.5	186	120	39	100.0	-1.3
185	6.0	1.9	73.2	-5.9					

We see that the rotation remains sensibly constant up to 2.3 half-lives, or 80% of reaction. It has fallen by only 10% after 8—9 half-lives, or 99.7% of reaction, when decomposition is beginning to be obvious. Most of it has gone after 39 half-lives when the decomposition has become extensive. Clearly, the fall of rotation at these late times is to do with the decomposition, and the exchange reaction itself has no effect on rotation. We conclude that configuration is fully preserved in this exchange reaction.

(6) *Mechanism of the Uncatalysed One-alkyl Substitution.*—The kinetic results of Sections 2 and 3 show that all the mercury-exchange reactions considered in this paper

exemplify the one-alkyl substitution anticipated in Part I.⁶ The same data show that this electrophilic substitution proceeds in a single step of unit order in each reactant, whilst the polarimetric results of Section 5 establish that in that step configuration is fully preserved. These findings agree in excluding mechanism S_{E1} , and in permitting either mechanism S_{E2} or mechanism S_{Ei} . The problem remains of distinguishing between these two mechanisms: we have a bimolecular transition state, and have to decide whether it is an open or a closed one.

The simplest test of that matter is to increase the ionicity of the interacting salts and note the effect of so doing on the absolute rate. We find that from halides to acetate, and thence to nitrate, the rate increases sharply, indeed by factors of 10^2 — 10^3 at each step. This will be clear from the summary in Table 5 of second-order rate-constants for one-alkyl substitution, which establish the rate sequence, $\text{MeHgBr} < \text{MeHgI} \ll \text{MeHg}\cdot\text{OAc} \ll \text{MeHg}\cdot\text{NO}_3$. It is thus shown that the reaction receives no important assistance from combination between the anion of the substituting agent and the mercury atom being expelled, or, in other words, that the transition state is an open one, apart from its solvation. This conclusion is confirmed by the kinetic salt effects next to be discussed, and, for the bromide reactions, by the results in the next paper, which show what does happen when we take steps calculated to close the transition state.

TABLE 5. *Summary of second-order rate-constants ($k_2^{(1)}$ in mole⁻¹ l. sec.⁻¹) in ethanol of the one-alkyl electrophilic substitutions, $\text{RHgX} + \overset{*}{\text{HgX}}_2 \longrightarrow \text{R}\overset{*}{\text{HgX}} + \text{HgX}_2$.*

R	X	$10^3 k_2^{(1)}$			Rel. rate
		100.2°	59.8°	0.0°	
Me	Br	12.8	0.50	0.0007 †	1
"	I	101	—	—	7.9
"	OAc	—	500	—	1000
"	NO ₃	—	—	169	240,000
Bu ^a	OAc	—	30.5	—	61

† Extrapolated from observed values at the higher temperatures.

The positive salt effects reported in Section 4 show that, for both the bromide and acetate reactions thus examined, the transition states are more polar than the initial states. Thus, 0.1M of added lithium nitrate increases the rate of the former reaction by a factor of about 2.5, and of the latter by one of about 1.5. In the bromide reaction, the initial state is relatively non-polar, but the transition state must be much more polar. Furthermore, the semilogarithmic linearity of this salt effect suggests that the extra polarity of the transition state is one of stronger dipoles,^{10,11} rather than of newly produced free ions. In the reaction of the more ionic acetates, the initial state is moderately polar, and the transition state is more polar still, but by a smaller margin than before. The functional form of the salt effect is now intermediate between those expected for ion-dipole and ion-ion interaction, and may be indicating that in the transition state, not only are dipoles further strengthened, but also rather more free ions are produced. All this is much easier to understand on the basis of an open than on that of a closed transition state.

Because of their analogous electrostatic origins, normal salt effects and polar co-solvent effects usually follow each other qualitatively, in the absence of specific effects, though differences of functional form will arise, if only because co-solvents must act at closer ranges than those at which salts may act. It is shown in Section 2 that the addition of water to the ethanolic solvent does accelerate the bromide reaction. But 10 vols. % of water raised the rate by a factor of only 1.8, an amount which, having regard to the considerable magnitude of the salt effect on the bromide reaction, seems small, until it is

¹⁰ Kirkwood, *Chem. Rev.*, 1939, **24**, 2330.

¹¹ Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 983.

recollected that a countervailing specific effect of water is expected, which has to be overcome. For it is fairly certain that water specifically co-ordinates with mercuric halides,¹² perhaps four molecules of water, to give octahedral structures. Thus the formation of the transition state will necessitate a partial de-aquation, which, being endothermic, should of itself retard reaction.

The summary of these conclusions is that all the mercury exchanges here considered of simple alkylmercuric halides, acetates, and nitrates, with corresponding mercuric salts, exemplify the anticipated one-alkyl electrophilic mercury-for-mercury substitution, which proceeds by mechanism S_E2 , with full retention of configuration.

EXPERIMENTAL

Materials.—Most of our methylmercuric bromide was prepared from methylmagnesium bromide and mercuric bromide, but some was made from dimethylmercury and mercuric bromide. The product obtained in either way had m. p. 161—162° (Found: C, 4.16; H, 0.95; Br, 27.2. Calc. for CH_3BrHg : C, 4.06; H, 1.02; Br, 27.1%). Nefedov and his co-workers² record m. p. 172°. We tried crystallisation from ethanol, methanol, ether, and benzene, and steam-distillation and sublimation, as alternative or successive methods of purification, but could not raise our m. p. above 161—162°, which essentially agrees with the m. p., 160°, recorded by earlier workers.^{13,14} Our methylmercuric iodide was a gift from Imperial Chemical Industries Limited, through the courtesy of Dr. W. B. Waddington (Huddersfield): crystallised from ethanol, it had m. p. 144°. The acetate was made from dimethylmercury and mercuric acetate:¹⁵ after sublimation it had m. p. 128—129°. *s*-Butylmercuric acetate was prepared analogously:⁸ crystallised from pentane, it had m. p. 29°. The optically active salt was similarly obtained from optically active di-*s*-butylmercury.⁷ Methylmercuric nitrate was prepared from methylmercuric bromide and silver nitrate:¹⁶ crystallised from ether-pentane, it had m. p. 58—59°.

Radiomercuric oxide containing only ²⁰³Hg and stable isotopes was converted with aqueous hydrobromic acid into radiomercuric bromide, which was crystallised from ethanol. Radiomercuric iodide was precipitated by potassium iodide from a solution of the oxide in aqueous nitric acid and was crystallised from aqueous dioxan. Radiomercuric acetate was made by dissolving the oxide in nitric acid, precipitating the hydrated oxide with potassium hydroxide, and dissolving the well-washed precipitate in dilute acetic acid, from which the acetate was crystallised. Radiomercuric nitrate was obtained by crystallisation from a solution of the oxide in aqueous nitric acid. The acetate and nitrate were dried in a vacuum over potassium hydroxide. Ethanol was dried by the method which uses ethyl phthalate.

Rates of Mercury Exchange.—Kinetics of the exchanges with bromides and iodides were followed by the sealed-tube method. The reaction solution was made up at 20°, and a charge of 10 ml. was enclosed in each tube. The tubes were placed in a thermostat, and, from time to time, one was transferred to a freezing-mixture. After an investigation of methods of separating alkylmercuric salts from mercuric salts, without entrainment of the latter, and without exchange during separation, a general procedure was evolved, which had to be modified slightly from case to case. For the exchange with methylmercuric bromide, the salts which had crystallised in the cooled tube, were, after opening of the tubes, caused to redissolve by heating to 20—30°. The solution was then poured through glass-wool into a continuously stirred 5% solution of potassium bromide in 50% aqueous ethanol. Pure methylmercuric bromide (m. p. and mixed m. p. 161—162°) was thus precipitated, usually at once, or, if not, after the addition of a little ice-water. For the exchange with methylmercuric iodide, it was found advisable to add some potassium iodide to the contents of the cooled tube, and then to complete re-dissolution by heating to 20° before pouring through glass wool into a stirred 10% solution of potassium iodide in 50% aqueous ethanol, pure methylmercuric iodide being precipitated.

The kinetic runs with acetates and nitrates were conducted in flasks, in which solutions

¹² Van Panthaleon van Eck, Thesis, Leiden University, 1958.

¹³ Crymble, *J.*, 1914, **105**, 667.

¹⁴ Vaughan, Spahr, and Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 4206.

¹⁵ Sneed and Maynard, *J. Amer. Chem. Soc.*, 1922, **44**, 2942.

¹⁶ Johns, Peterson, and Hixon, *J. Amer. Chem. Soc.*, 1930, **52**, 2820.

of the reactants, made separately at the reaction temperature, were mixed at that temperature. As methylmercuric nitrate is solvolysed in neutral ethanol, a small amount of nitric acid was added in the nitrate exchanges in order to obviate this difficulty. After known times in the thermostat, samples of 10 ml. were withdrawn to be run into empty tubes cooled with solid carbon dioxide-acetone. This method of quenching was shown to be adequate even for the rapid nitrate exchanges. For the acetate and the nitrate exchanges, the method of separation was as follows. To each cooled sample, 10 ml. of 10% aqueous potassium bromide were added. The precipitated mixture of methyl- or s-butyl-mercuric bromide and mercuric bromide was collected, washed, and dissolved in acetone. This solution was poured with stirring into 10 ml. of 10% aqueous potassium bromide, pure methyl- or s-butyl-mercuric bromide being precipitated.

Weighed amounts of the recovered samples of methylmercuric bromide or iodide or s-butylmercuric bromide were dissolved each in 10 ml. of acetone, and the counts of radiation from these solutions were measured with precautions and corrections mentioned in the preceding paper.

The various rate-constants obtained by these methods are listed in Tables 1, 2, and 3. The methylmercuric bromide and iodide reactions at 100.2° were followed to about 70–85% of the possible extent of exchange, but the methylmercuric bromide reaction at 59.8° was followed only to 50–60% because appreciable decomposition set in during the long periods (weeks) needed to follow the reaction much further at this temperature. The methylmercuric acetate and nitrate reactions were followed to 70–80% of the possible amount of exchange: there was detectable decomposition in the later stages of these reactions, but not enough appreciably to affect the kinetics within the stated range. For the slower reactions of the s-butylmercuric salts, decomposition was generally more pronounced, and, for s-butylmercuric bromide and iodide, it made our rate-measurements too inaccurate to be quoted. However, the moderately fast reaction of s-butylmercuric acetate was followed up to 70–80% of the possible exchange (and the work of Section 5 suggests that it could probably have been followed somewhat further) without sensible disturbance from decomposition, though, here again, decomposition becomes considerable after long periods. It remains to record a few specimen runs, and this is done in Table 6.

TABLE 6. *Specimen runs.*

(In all runs the radioactivity was initially in a mercuric salt; and it was measured in samples of an alkylmercuric salt recovered after known reaction-times. The units of $k_2^{(1)}$ are mole⁻¹ l. sec.⁻¹. These constants are corrected for the volume change of the solvent when the temperatures at which concentrations were set, and at which the reaction was conducted, were different.)

Run 30: [MeHgBr] = 0.100M, [HgBr ₂] = 0.200M, at 20°; reaction in ethanol at 100.2°.				Run 117: [Bu ^s HgOAc] = 0.325M, [Hg(OAc) ₂] = 0.104M, at 60°; reaction in ethanol at 59.8°.			
Time (hr.)	Count (min. ⁻¹ , corr.)	Reaction (%) = 100 (1 - f)	10 ⁵ k ₂ ⁽¹⁾ (corr.)	Time (min.)	Count (min. ⁻¹ , corr.)	Reaction (%) = 100 (1 - f)	10 ⁵ k ₂ ⁽¹⁾
0	44.6	9.2	—	0	142.2	22.2	—
1	94.6	19.5	13.2	30	250.8	38.8	31.4
2	140.7	29.0	13.0	60	340.0	52.6	32.2
3	185.2	38.2	13.4	90	453.0	63.9	33.3
4	223.2	46.0	13.4	120	464.1	71.8	33.0
5	253.2	52.2	13.2				
8	327.8	67.6	13.2				
Mean: 13.2				Mean: 33.5			

Run 87: [MeHg·NO₃] = 0.185M, [Hg(NO₃)₂] = 0.233M at 0°; reaction in ethanol containing 0.32M-nitric acid and 0.47M-water at 0.0°.

Time (min.)	Count, MeHgBr (min. ⁻¹ , corr.)	Reaction (%) = 100 (1 - f)	10 ⁵ k ₂ ⁽¹⁾
8	105.2	26.4	(156)
12	155.3	39.0	168
18	216.1	54.3	177
25	268.3	67.3	182
34	306.8	77.1	177

Mean: 176

Polarimetric Changes accompanying Mercury Exchange.—The optically active s-butylmercuric acetate (above) had $[\alpha]_D^{20} - 4.5^\circ$, and the bromide obtained from it $[\alpha]_D^{20} - 5.7^\circ$ ($c = 4$,

in acetone). The conditions of the runs with the optically active acetate are specified in Section 5. From timed samples of 25 ml., rapidly cooled, and mixed with 25 ml. of 10% aqueous potassium bromide, *s*-butylmercuric bromide was precipitated, which was washed with potassium bromide solution, and with water, and, when dry, crystallised from pentane, before its rotation ($l = 2$ dm.) was measured in acetone ($c = 4$). The specific rotations, thus obtained after various reaction times in ethanol at 59.8° , are listed in Table 4.

A Ramsay Fellowship held by one of us (H. C. V.) is gratefully acknowledged.

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[Received, September 20th, 1960.]
