# 226. *Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part III.*[1] *Kinetics, Stereochemistry, and Mechanism of the Three-alkyl Mercury-exchange Reaction.*

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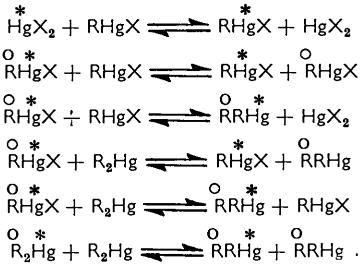
It is shown that mercury-for-mercury replacement in the reactions of s-butylmercuric bromide, acetate, and nitrate, severally, with di-s-butylmercury in ethanol is the anticipated, but observationally new, three-alkyl substitution, proceeding by the bimolecular electrophilic mechanism $S_E2$, in which stereochemical configuration is fully preserved. That this three-alkyl electrophilic exchange is indeed under observation, rather than any other process or combination of processes of alkyl-redistribution that might have simulated its stoicheiometry, is shown both by double-labelling, using the labels of optical activity and radioactivity in conjunction and alternatively, and by a study of kinetic form. That the substitution fully preserves configuration is shown both by the polarimetrically followed kinetics, and by the final rotations of products from " spent " runs. That, of the two mechanisms, $S_E2$ and $S_Ei$, which are both consistent with both the second-order kinetic form and the retention of configuration, the one actually observed is mechanism $S_E2$, is shown both by the great increase of rate with increasing ionicity of the substituting agent, and by the positive kinetic effects of added lithium salts, which, lithium bromide not excepted, act broadly according to the ease of their ionic dissociation, and independently of the nature of the s-butylmercuric substituting agent, in the range studied.

(1) *Introduction to Parts* III—V.—As explained in Part I,[2] we have entered on the study of electrophilic substitution at saturated carbon by way of the redistribution reactions of alkylmercury compounds, because replacement of mercury by mercury allows the stereochemical part of the mechanistic evidence to be presented without the assumptions involved in assigning configurations to the optical isomers with which we deal when one element is being replaced by another. There are six conceivable redistribution reactions, (*a*)—(*f*) below, and we shall be concerned with problems of distinguishing between them, when, either in one step or more than one, several could lead to an identical overall stoicheiometry. The labels on R and Hg are at this stage attached only for clarity: in experimental work one does not always need all of them:



Exch. R *v.* X $\overset{*}{\mathrm{Hg}}\mathrm{X_2} + \mathrm{RHgX} \rightleftharpoons \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{HgX_2}$ . . . . . . (*a*)

,, R *v.* R $\overset{\circ}{\mathrm{R}}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{RHgX} \rightleftharpoons \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} + \overset{\circ}{\mathrm{R}}\mathrm{HgX}$ . . . . . . (*b*)

,, R *v.* X $\overset{\circ}{\mathrm{R}}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{RHgX} \rightleftharpoons \overset{\circ}{\mathrm{R}}\mathrm{R}\overset{*}{\mathrm{Hg}} + \mathrm{HgX_2}$ . . . . . . (*c*)

,, R *v.* R $\overset{\circ}{\mathrm{R}}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{R_2Hg} \rightleftharpoons \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} + \overset{\circ}{\mathrm{R}}\mathrm{RHg}$ . . . . . . (*d*)

,, R *v.* X $\overset{\circ}{\mathrm{R}}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{R_2Hg} \rightleftharpoons \overset{\circ}{\mathrm{R}}\mathrm{R}\overset{*}{\mathrm{Hg}} + \mathrm{RHgX}$ . . . . . . (*e*)

,, R *v.* R $\overset{\circ}{\mathrm{R}}_2\overset{*}{\mathrm{Hg}} + \mathrm{R_2Hg} \rightleftharpoons \overset{\circ}{\mathrm{R}}\mathrm{R}\overset{*}{\mathrm{Hg}} + \overset{\circ}{\mathrm{R}}\mathrm{RHg}$ . . . . . . (*f*)

Theoretically, only the redistributions (*a*), (*c*), and (*e*) can be formulated as electrophilic substitutions. These one-, two-, and three-alkyl exchanges, as we call them, are so formulated in (1)—(3) below. However, it is a matter for experimental demonstration whether they all, and they alone, exist as independent processes. The two-alkyl reaction was well known so to do, and, on that foundation, we developed in Part II[1] a study of its kinetics and stereochemistry in correlation. It was mentioned there that the three- and

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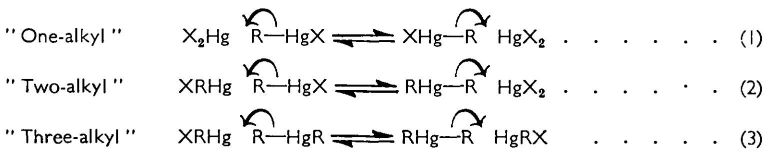
[1] Part II, Charman, Hughes, and Ingold, *J.*, 1959, 2530.

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

one-alkyl exchanges, on which we now report, had been identified and investigated similarly.[3]



$$\text{" One-alkyl "} \quad X_2Hg \;\; R{-}HgX \rightleftharpoons XHg{-}R \;\; HgX_2 \qquad (1)$$

$$\text{" Two-alkyl "} \quad XRHg \;\; R{-}HgX \rightleftharpoons RHg{-}R \;\; HgX_2 \qquad (2)$$

$$\text{" Three-alkyl "} \quad XRHg \;\; R{-}HgR \rightleftharpoons RHg{-}R \;\; HgRX \qquad (3)$$

(2) *Three-alkyl Exchange: Identification by Double-labelling.*—No alkylmercury redistribution which might be the three-alkyl exchange has been described before.* Unlike the two-alkyl substitution, whose factors and products are always different, observation of the three-alkyl exchange requires distinctions either between the alkyl groups or between the mercury atoms. Having available optically active s-butylmercuric salts,† we could introduce a label of optical activity on an alkyl group, and follow alkyl exchange with di-s-butylmercury by following movement of the optical label. With s-butylmercuric bromide, for example, such movement does take place at a convenient rate in ethanol at 35°.

Now this result might arise from any of three of the above redistribution reactions, *viz.*, from a single step of reaction (*e*), a single step of reaction (*d*), or a combination of forward and backward steps of the well-known reaction (*c*). A possibility of distinguishing between these alternatives arises, if we introduce additionally a label of radioactivity on one of the mercury atoms, as with $^{203}Hg$, and follow alkyl exchange and mercury exchange side by side. This can be seen from the following equations, in which Bu means s-Bu, the degree-sign signifies a label of optical activity, and the asterisk one of radioactivity. In a single step of reaction (*e*),

$$\overset{\circ}{Bu}\overset{*}{Hg}Br + Bu_2Hg \longrightarrow \overset{\circ}{Bu}Bu\overset{*}{Hg} + BuHgBr \qquad (4)$$

one mercury label is transferred, for each alkyl label that is transferred, from one chemical species to the other; *i.e.*, the ratio, mercury-exchange/alkyl-exchange = 1. In a single step of reaction (*d*),

$$\overset{\circ}{Bu}\overset{*}{Hg}Br + Bu_2Hg \longrightarrow Bu\overset{*}{Hg}Br + \overset{\circ}{Bu}BuHg \qquad (5)$$

no mercury label is transferred when an alkyl label is thus transferred; *i.e.*, the ratio, mercury-exchange/alkyl-exchange = 0. In a composition of two steps of reaction (*c*),

* [*Added in proof.*] Except in the preliminary record of this work.[3] But since the present paper was written, a preliminary account of such a reaction between optically active 2-methylhexane-5-mercuric bromide and di(2-methylhexyl-5-)mercury has been given by Reutov and his co-workers.[3a] In both accounts, the method was that of double labelling (*vide infra*), and the conclusions derived by that method were identical.

† Since we described the resolution of butane-2-mercuric (*i.e.*, s-butylmercuric) salts through the mandelate,[4] we have described it through the normal tartrate,[2] and Reutov and Uglova have reported resolutions of both butane-2- and 2-methylhexane-5-mercuric salts through their ethyl tartrates.[5] Jensen *et al.* have recently [6] redescribed the original resolution of butane-2 salts through the mandelate. They refer in a footnote to our account of two years earlier as one of a " partial resolution," omitting to mention that our originally recorded highest rotation of the bromide ($[\alpha]_D^{20}$ −24·0°, $c$ = 5, in acetone) was quite close to the maxima they now give ($[\alpha]_D$ −24·0° to −25·9° in various other polarimetric conditions).

Both the other groups of authors have used their optically active materials to confirm the retention of configuration, which we established, with kinetic control of the conditions, in Part II,[1] in the two-alkyl conversion of a dialkylmercury with mercuric bromide to an alkylmercuric bromide. Reutov and Uglova did this [7] with their 2-methylhexane-5-derivative, and Jensen has now done it,[8] exactly as we did, except that he omits kinetic control, using the butane-2-compound. The optical results (ratios of rotations of factors and products) of these three investigations agree perfectly.

[3] Charman, Thesis, London University, 1958.

[3a] Reutov, Karpov, and Uglova, *Tetrahedron Letters*, 1960, No. 19, 6.

[4] Charman, Hughes, and Ingold, *Chem. and Ind.*, 1958, 1517.

[5] Reutov and Uglova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 757.

[6] Jensen, Whipple, Wedegaertner, and Landgrebe, *J. Amer. Chem. Soc.*, 1960, **82**, 2466.

[7] Reutov and Uglova, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1959, 1691.

[8] Jensen, *J. Amer. Chem. Soc.*, 1960, **82**, 2469.

mercuric bromide would be produced in the first step but consumed in the second, and thus would not enter into the overall stoicheiometry:

$$\left.\begin{array}{l}\overset{\circ}{\text{Bu}}\overset{*}{\text{Hg}}\text{Br} + \overset{\circ}{\text{Bu}}\overset{*}{\text{Hg}}\text{Br} \longrightarrow \overset{\circ}{\text{Bu}}_2\overset{*}{\text{Hg}} + \overset{*}{\text{Hg}}\text{Br}_2 \\ \overset{*}{\text{Hg}}\text{Br}_2 + \text{Bu}_2\text{Hg} \longrightarrow \text{Bu}\overset{*}{\text{Hg}}\text{Br} + \text{BuHgBr}\end{array}\right\} \quad \ldots\ldots\ldots \quad (6)$$

The net result is that one mercury label is transferred when two alkyl labels are transferred from one chemical form to the other, *i.e.*, that the ratio, mercury-exchange/alkyl-exchange = $\frac{1}{2}$.

We made the twice-labelled alkylmercuric salt by an application of the exchange reaction which forms the subject of the two following papers: optically active s-butylmercuric bromide was brought to equilibrium with radioactive mercuric bromide, so that the resulting s-butylmercuric bromide had become labelled in both ways:

$$\overset{\circ}{\text{Bu}}\text{HgBr} + \overset{*}{\text{Hg}}\text{Br}_2 \rightleftharpoons \overset{\circ}{\text{Bu}}\overset{*}{\text{Hg}}\text{Br} + \text{HgBr}_2$$

The product had a specific optical rotation (measured, as is done throughout this work, with $l = 2$ dm.) of $[\alpha]_D^{20}$ $-14{\cdot}5°$ ($c = 5$, in acetone), *i.e.*, 60% of the maximum, and a radioactivity, due to $^{203}$Hg, which, of course, fell slowly from day to day (the half-life is 46·5 days), but, in concentrations up to 0·1M in acetone, gave counts of the order of 10,000 in periods up to 1 hr. The radioactivity of this initial material was always measured on the same day as that of each timed sample from a kinetic experiment, such as that (run 1) now to be described.

A solution, 0·1M in the twice-labelled s-butylmercuric bromide, and 0·1M in unlabelled di-s-butylmercury, in solvent ethanol, was set at 35°; and, at times up to 65 hours, when 85% of the possible exchange had occurred, samples were taken for measurement of the radioactivity and the optical activity in separated s-butylmercuric bromide. (The change of optical activity was thereafter followed for much longer, for a reason explained in Section 3.) The rate of mercury exchange, as determined by the transfer of radioactivity, was $4{\cdot}4 \times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$. The rate of alkyl exchange, as given by the change of optical activity, was $4{\cdot}6 \times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$. Thus the ratio, mercury-exchange/alkyl-exchange, was 0·96, *i.e.*, unity to within the experimental error.

It follows that the reaction under observation is that of equation (4), *i.e.*, it exemplifies the three-alkyl electrophilic substitution (*e*) or (3)—a new reaction. It cannot be the reaction of equation (5), which would exemplify the non-electrophilic redistribution process (*d*); for that should produce no mercury exchange. The composition, represented in equations (6), of two steps of the known two-alkyl electrophilic substitution (*c*) or (2), is nearly as thoroughly excluded by the above result; and we shall confirm its exclusion, both by a modification of the same method, and by a completely independent method, in Section 4.

It is necessary to understand the meaning of exchange-rate figures, such as those quoted above. The relevant formulæ are included in an Appendix dealing mainly with a more complicated situation than that described above. However, the matter can be appreciated less formally.

In a mixture of constant composition at constant temperature, any exchange, apart from labels, of what we may call an exchangeable "residue," *i.e.*, any atom or group that does exchange, goes on for ever at a constant rate. This zeroth-order rate, $k_0$, is equal to the measurable *initial* rate of transfer of the residue from a chemical species in which, uniquely, it was originally labelled—the "initial rate of label-transfer," as we may say,—"initial," because it must apply to the period before labelled and unlabelled residues become mixed in the same chemical species. The observable label-transfer in the sense defined will be a first-order process, the ultimately possible extent of which, reckoned as a fraction of the total labelled-residue concentration, is just the ratio of unlabelled to total residues, *e.g.*, $\frac{1}{2}$ for mercury, and $\frac{2}{3}$ for alkyl, in the above-described experiment. If, at time $t$, a fraction $f$ of the ultimate amount of transfer has still to occur, the first-order rate-constant for label-transfer will, of course, be $k_1 = -(1/t) \ln f$. By definition, this is the rate, $-\mathrm{d}f/\mathrm{d}t$, at $t = 0$. If now we multiply the " initial rate of label-transfer " in this form by the denominator of the fraction $f$, *i.e.*, by the concentration of label ultimately transferable—in the above example, by $\frac{1}{2}$ or $\frac{2}{3}$, as the case may be, of the concentration, 0·1M, of the originally labelled compound—we shall have the initial rate in concentration units, $-\mathrm{d}c/\mathrm{d}t$, at $t = 0$. And this is the constant rate of exchange, $k_0$, of the residue, apart altogether from labels.

(3) *Stereochemical Course of the Three-alkyl Substitution.*—This is shown, first of all, by the experiment already described. For unless the label of optical activity "stuck" firmly to its alkyl group, while this was being passed about from one chemical species to the other, rates of alkyl exchange, $k_0^{\mathrm{Alk}}$, computed as described from observations of optical activity made at different times during the run, would not be consistent. Good consistency has, however, been obtained in all runs followed by the optical method as illustrated in the Experimental section in Table 8. Most of these runs lack a simultaneously present label of radioactivity, and are reported in summary in this Section and the following one.

Still more forcibly, the firm " sticking " of the optical label is proved by the fact that the final irreducible rotation of the s-butylmercuric bromide recovered from " spent " runs, after periods of the order of 20 half-lives, is one-third of the initial rotation of that substance; and one-third is the ratio of labelled to total alkyl groups. Thus, in the doubly-labelled run described above (run 1), the rotation of the s-butylmercuric bromide, $[\alpha]_D^{20}$ ($c = 5$, in acetone), fell from an initial $-14·5°$ to a final $-4·7°$. This result, and some similar ones obtained with singly-labelled runs which were followed over long periods (weeks), are collected in Table 1.

TABLE 1. *Initial and final rotations* ($[\alpha]_D^{20}$, $c = 5$, *in acetone*) *of s-butylmercuric bromide, and exchange rates* ($k_0^{\mathrm{Alk.}}$ *in mole l.*$^{-1}$ *sec.*$^{-1}$), *in polarimetrically followed exchanges with di-s-butylmercury in ethanol at* 35·0°.

| No. | $[\mathrm{Bu^sHgBr}] = [\mathrm{Bu^s_2Hg}]$ | [LiBr] | Rotations Initial | Final | No. of $\frac{1}{2}$-lives followed | $10^7 k_0$Alk |
|---|---|---|---|---|---|---|
| 1 | 0·1 | — | −14·5° | −4·7° | 14 | 4·6 |
| 3 | 0·1 | — | −12·15 | −3·95 | 19 | 4·7 |
| 4 | 0·1 | — | −12·2 | −4·0 | ~20 | 4·8 |
| 7 * | 0·1 | 0·1 | −10·2 | −3·25 | 28 | 10·1 |

* It is shown in a separate experiment that lithium bromide, although it accelerates the exchange and therefore the fall of rotation, does not cause racemisation of s-butylmercuric bromide in the absence of s-dibutylmercury, in otherwise the same conditions.

All this proves that the three-alkyl substitution proceeds with total retention of configuration. If it were accompanied by partial or complete racemisation, the rotation of the s-butylmercuric bromide would fall to zero. If it proceeded with configurational inversion, even total inversion, the rotation would still fall to zero.

(4) *Kinetics of the Three-alkyl Substitution.*—Our first concern was to confirm the identification (Section 2) of the reaction of s-butylmercuric bromide with di-s-butylmercury as a three-alkyl electrophilic substitution (3); and, as to this, we did two things. The first was to generalise the double-labelling method. For the principle, by which the exchange reaction may be identified according to whether the ratio, mercury-exchange/alkyl-exchange, is unity, one-half, or zero, can obviously be applied, not only, as we did it originally, by simultaneous double-labelling, but also by putting the alternative labels into parallel experiments. Our comparison of exchange rates with this generalisation of method is set out in Table 2. One sees that the rate of exchange, whether of mercury measured by radioactivity, or of alkyl followed by optical activity, is the same; and that therefore, by this test, the process is indeed the substitution (3).

In our radiometric measurements generally, we sometimes put the radiomercury ($^{203}$Hg) originally into the s-butylmercuric bromide, and sometimes into the di-s-butylmercury, the latter substance being made from the former by the Grignard method. In the experiments of Table 2, the radioactivity was originally in the s-butylmercuric bromide.

TABLE 2. *Rates of exchange of alkyl and mercury* ($k_0^{\text{Alk}}$ *and* $k_0^{\text{Hg}}$ *in mole l.*$^{-1}$ *sec.*$^{-1}$) *between s-butylmercuric bromide* (0·1M) *and di-s-butylmercury* (0·1M) *in ethanol at* 35·0°

| By optical activity | | | By radioactivity | | |
|---|---|---|---|---|---|
| Run | $10^7k_0^{\text{Alk}}$ | Mean | Run | $10^7k_0^{\text{Hg}}$ | Mean |
| 1 | 4·6 | 4·7 | 1 | 4·4 | 4·6 |
| 3 | 4·7 | | 54 | 4·9 | |
| 4 | 4·8 | | 57 | 4·4 | |

A second kinetic method has been applied to the distinction between the three-alkyl substitution (3) and its simulation by two steps of the known two-alkyl substitution (2). The principle is as follows. A zeroth-order rate of exchange will usually depend on the concentrations of the exchanging species. The nature of the dependence will not necessarily be indicated by the kinetic forms of the observed label-transfers, because these will be of first order whatever the mechanism of exchange, if no reactions other than exchange are going on. However, the form of the dependence can be found by varying the concentrations of the reactants, which are, of course, constants of the individual experiments. If, independently of the degree of labelling, $a$ is the concentration of s-butylmercuric bromide, and $b$ is that of the di-s-butylmercury, and if $k_0$ is the rate of exchange as measured by the rate of transfer of either of our labels, then, supposing that exchange proceeds in a single step, as of substitution (3) exemplified by equation (4), we should find that a second-order rate-constant, defined by the equation $k_2^{(3)} = k_0/ab$, would be invariant with changing $a$ and $b$, apart from medium effects. However, if exchange occurs through two successive steps of substitution (2), *i.e.*, two reversible processes of label-transfer, as illustrated in equations (6), then one can show that another second-order rate-constant of substitution, $k_2^{(2)} = k_0/a^2$, should be invariant with changing $a$ and $b$, except for medium effects. As is shown in the Appendix (p. 1132), these relations hold, according to mechanism, without making any difference to the form of the time-dependent observations from which the label-transfer rate-constant $k_1$, and thence the exchange rate $k_0$, are derived, as explained in Section 2.

A determination of the dependence of $k_0$ on $a$ and $b$ constitutes, not only a confirmatory test of our identification of the chemical nature of the substitution, but also a first essential contribution to the kinetic elucidation of its mechanism. For it is a test of whether the reaction goes in one step or more than one. If it goes in one step, then it must be the three-alkyl substitution, with a mechanism of molecularity two. However, the three-alkyl substitution could conceivably occur by way of a slow ionisation of the dialkylmercury, *i.e.*, by a mechanism of molecularity one. Actually our optical result (Section 3), that configuration is completely retained in the substitution, goes far to exclude this interpretation; but if it were true, the kinetic consequence would be that, medium effects apart, yet another rate-constant of substitution, a first-order one, $k_1^{(3)} = k_0/b$, would be invariant with changing $a$ and $b$, again without alteration to the form of the time-dependent observations.

The results of these measurements, made with mercury-labelling, are in Table 3. They confirm that the reaction is not a composition of steps of the two-alkyl substitution, but is a three-alkyl substitution, which, moreover, proceeds in one bimolecular step. The rate of exchange, $k_0^{\text{Hg}}$, obviously varies systematically with the concentrations of both reactants. The rate-constants of substitution, $k_2^{(2)}$ and $k_1^{(3)}$, also vary with the concentration of at least one of the reactants. The substitution rate-constant, $k_2^{(3)}$, is, however, relatively steady. Most of the variation in its individual values can be assigned to experimental error, though the apparent small rise with the concentration of s-butylmercuric bromide may well be genuine, and, if so, may be a medium effect: we demonstrate below the kinetic effect of certain added lithium salts.

Salt effects on this reaction were examined in order to provide further evidence of mechanism. The effect of added lithium salts on the second-order rate-constant of substitution, $k_2^{(3)}$, is generally one of acceleration. In the case of lithium acetate the effect was very small indeed, not quite clearly outside the experimental error. Lithium nitrate produced a somewhat small, but definitely demonstrable effect, lithium bromide a larger one, and lithium perchlorate a somewhat larger one still. All these accelerating effects are trifling compared to some we shall have to consider in Part V (accompanying). In the example of lithium bromide, we examined the form of the dependence of the rate-increase on the concentration of the added salt: the logarithm of the rate increased with a power of the concentration, which was less than one, but more than one-half. Some of these measurements were made radiometrically, by way of the rate of mercury exchange $k_0^{\mathrm{Hg}}$, and others polarimetrically, through the rate of alkyl exchange $k_0^{\mathrm{Alk.}}$. The results are in Table 4. They are discussed in Section 5.

TABLE 3. *Radiometrically measured rates of mercury exchange* ($k_0^{\mathrm{Hg}}$, *in mole l.*$^{-1}$ *sec.*$^{-1}$) *and first-order* ($k_1^{(3)}$ *in sec.*$^{-1}$) *and second-order* ($k_2^{(2)}$ *and* $k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *rate-constants of substitution by s-butylmercuric bromide* (*concentration a*) *in di-s-butylmercury* (*concentration b*) *in ethanol at* 35·0°.

| Run | *a* (M) | *b* (M) | $10^7k_0^{\mathrm{Hg}}$ | $10^5k_2^{(2)}$ | $10^6k_1^{(3)}$ | $10^5k_2^{(3)}$ |
|---|---|---|---|---|---|---|
| 1 | 0·1 | 0·1 | 4·4 | 4·4 | 4·4 | 4·4 |
| 54 | 0·1 | 0·1 | 4·9 | 4·9 | 4·9 | 4·9 |
| 57 | 0·1 | 0·1 | 4·4 | 4·4 | 4·4 | 4·4 |
| 49 | 0·12 | 0·1 | 6·0 | 4·2 | 6·0 | 5·0 |
| 50 | 0·14 | 0·1 | 7·5 | 3·8 | 7·5 | 5·4 |
| 78 * | 0·1 | 0·06 | 2·4 | 2·4 | 4·0 | 4·0 |
| 46 | 0·1 | 0·15 | 7·9 | 7·9 | 5·3 | 5·3 |
| 51 | 0·1 | 0·18 | 7·8 | 7·8 | 4·3 | 4·3 |

* In this experiment, the radiomercury was initially in the di-s-butylmercury; in all others of this Table, it was initially in the s-butylmercuric bromide.

TABLE 4. *Effects of added lithium salts on the second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *by s-butylmercuric bromide* (0·1M) *in di-s-butylmercury* (0·1M) *in ethanol at* 35·0°.

| Run | [Salt] | $10^5k_2^{(3)}$ | Mean | Run | [Salt] | $10^5k_2^{(3)}$ | Mean |
|---|---|---|---|---|---|---|---|
| *Lithium acetate* (*radiometric*) | | | | *Lithium bromide* (*polarimetric*) | | | |
| 1, 54, 57 | 0·0 | 4·4—4·9 | 4·6 | 1, 3, 4 | 0·0 | 4·6—4·8 | 4·7 |
| 55 | 0·1 | 5·6 | 5·0 | 12 | 0·025 | 6·2 | 6·2 |
| 56 | 0·1 | 5·5 | | 8 | 0·05 | 7·7 | 7·9 |
| 58 | 0·1 | 4·8 | | 7 | 0·1 | 10·1 | 10·0 |
| 69 * | 0·1 | 4·7 | | 10 | 0·1 | 10·0 | |
| 73 * | 0·1 | 4·6 | | 9 | 0·125 | 11·2 | 11·2 |
| | | | | 11 | 0·2 | 14·8 | 14·8 |
| *Lithium nitrate* (*radiometric*) | | | | *Lithium perchlorate* (*polarimetric*) | | | |
| 1, 54, 57 | 0·0 | 4·4—4·9 | 4·6 | 1, 3, 4 | 0·0 | 4·6—4·8 | 4·7 |
| 70 * | 0·1 | 5·9 | 6·0 | 22 | 0·1 | 11·7 | 12·0 |
| 71 * | 0·1 | 6·1 | | 23 | 0·1 | 12·4 | |
| 72 * | 0·1 | 6·1 | | 24 | 0·1 | 11·8 | |
| 76 * | 0·15 | 7·5 | 7·5 | 25 | 0·1 | 11·9 | |

* In these experiments, the radiomercury was initially in the di-s-butylmercury; in all others on the left-hand side of this Table, it was initially on the s-butylmercuric bromide.

In the work of Part II on the two-alkyl mercury exchange,[1] useful evidence of the mechanism of the second-order reaction between mercuric salts and di-s-butylmercury was obtained by changing the anions of the salts: it was a significant result that substitution-rate increased along the anion series, bromide, acetate, nitrate, without disturbance to the kinetic form of substitution. Therefore our next proceeding was to investigate the kinetic effect of changing the anion of our s-butylmercuric substituting agent, from bromide, to acetate, and then to nitrate.

The three-alkyl substitution by s-butylmercuric acetate went considerably faster than by s-butylmercuric bromide. The reaction of the acetate was followed radiometrically in ethanol at 35°, with the radiomercury initially in the di-s-butylmercury:

$$\mathrm{BuHg{\cdot}OAc} + \mathrm{Bu_2\overset{*}{H}g} \rightleftharpoons \mathrm{Bu_2Hg} + \mathrm{Bu\overset{*}{H}g{\cdot}OAc}$$

The results are in Table 5. From the observed rate of mercury exchange, $k_0^{\mathrm{Hg}}$, we calculated the second-order rate-constant for the three-alkyl substitution, $k_2^{(3)}$. We did not prove directly that this is the correct rate-constant of substitution to calculate, but such proof is given, both (above) for the slower substitution of s-butylmercuric bromide, and (below) for the faster one of s-butylmercuric nitrate, wherefore it cannot be doubted that the same kinetics prevail throughout the series.

TABLE 5. *Radiometrically measured rates of mercury exchange ($k_0^{\mathrm{Hg}}$ in mole l.$^{-1}$ sec.$^{-1}$) between s-butylmercuric acetate and radiomercury-containing di-s-butylmercury and second-order rate-constants of substitution ($k_2^{(3)}$ in mole$^{-1}$ l. sec.$^{-1}$) in ethanol at* 35·0°.

| Run | [BuHg·OAc] = [Bu₂Hg] | $10^6k_0^{\mathrm{Hg}}$ | $10^4k_2^{(3)}$ | Mean |
|---|---|---|---|---|
| 80 | 0·1 | 2·9 | 2·9 | 2·7 |
| 81 | 0·1 | 2·7 | 2·7 | |
| 82 | 0·1 | 2·6 | 2·6 | |

The substitution by s-butylmercuric nitrate in di-s-butylmercury is much faster than either of the substitutions described above. The reaction of the nitrate was followed, like that of the acetate, by radiometric measurement of the rate of mercury exchange, the radiomercury being initially in the di-s-butylmercury:

$$\mathrm{BuHg{\cdot}NO_3} + \mathrm{Bu_2\overset{*}{H}g} \rightleftharpoons \mathrm{Bu_2Hg} + \mathrm{Bu\overset{*}{H}g{\cdot}NO_3}$$

The solvent was again ethanol, but, because of the high rates, the temperature was reduced to 0°, and even then the measurable exchange was over within a few minutes.

In this study, we varied the concentrations of the reactants independently, and, from the observed rates of mercury exchange, $k_0^{\mathrm{Hg}}$, we calculated the various possible rate-constants of substitution, *viz.*, the second-order constant, $k_2^{(2)}$, corresponding to a pair of steps of the two-alkyl process (2), and the first- and second-order constants, $k_1^{(3)}$ and $k_2^{(3)}$, representing different mechanisms of the three-alkyl substitution (3). The results, which are in Table 6, clearly exclude two-alkyl substitution and the first-order mechanism of three-alkyl substitution: the rate-constants representing these processes obviously vary systematically with one or both reactant concentrations. The only rate-constant of which the scatter is restricted to the order of magnitude of the observational uncertainty is the second-order three-alkyl constant $k_2^{(3)}$. Thus it is proved for the reaction of s-butylmercuric nitrate, as it has been for that of s-butylmercuric bromide, that the mechanism of substitution involves a single second-order step of the three-alkyl process (3).

Table 6 contains a suggestion that the second-order three-alkyl constant, $k_2^{(3)}$, increases a little with increasing concentration of s-butylmercuric nitrate. The effect seems somewhat larger than the experimental error. It may be a salt effect analogous to that, next to be described, of added lithium nitrate.

Our examination of salt effects on the reaction of s-butylmercuric nitrate was necessarily confined to salts which do not exchange their anion with the substituting agent to give a different one. Of the four salts used previously, only lithium nitrate and perchlorate were suitable for the present study: in fact, we used lithium nitrate. The addition of this salt mildly accelerated the substitution, as followed by mercury exchange, by s-butylmercuric nitrate. As shown in Table 7, the lithium salt, in concentration 0·15M, increased the second-order three-alkyl rate-constant, $k_2^{(3)}$, by about 1·5 times. This is nearly the same as the factor by which, as seen in Table 4, the same concentration of the same salt increases the rate of substitution by s-butylmercuric bromide in di-s-butylmercury. The significance of this and other salt effects is considered in Section 5.

TABLE 6. *Radiometrically measured rates of mercury exchange ($k_0^{\text{Hg}}$ in mole l.$^{-1}$ sec.$^{-1}$) and first-order ($k_1^{(3)}$ in sec.$^{-1}$) and second-order ($k_2^{(2)}$ and $k_2^{(3)}$ in mole$^{-1}$ l. sec.$^{-1}$) rate-constants of substitution by s-butylmercuric nitrate (concentration a) in radiomercury-containing di-s-butylmercury (concentration b) in ethanol at* 0·0°.

| Run | *a* (M) | *b* (M) | $10^4k_0^{\text{Hg}}$ | $10^2k_2^{(2)}$ | $10^3\,k_1^{(3)}$ | $10^2k_2^{(3)}$ | Mean |
|---|---|---|---|---|---|---|---|
| 67 | 0·04 | 0·1 | 1·1 | 6·9 | 1·1 | 2·8 | 2·8 |
| 68 | 0·04 | 0·1 | 1·1 | 6·9 | 1·1 | 2·8 | |
| 44 | 0·06 | 0·1 | 1·7 | 4·7 | 1·7 | 2·8 | 2·9 |
| 48 | 0·06 | 0·1 | 1·8 | 5·0 | 1·8 | 3·0 | |
| 60 | 0·08 | 0·1 | 2·5 | 3·9 | 2·5 | 3·1 | 3·4 |
| 66 | 0·08 | 0·1 | 3·0 | 4·7 | 3·0 | 3·7 | |
| 35 | 0·1 | 0·1 | 3·5 | 3·5 | 3·5 | 3·5 | 3·4 |
| 39 | 0·1 | 0·1 | 3·4 | 3·4 | 3·4 | 3·4 | |
| 41 | 0·1 | 0·1 | 3·3 | 3·3 | 3·3 | 3·3 | |
| 65 | 0·13 | 0·1 | 4·7 | 2·8 | 4·7 | 3·6 | 3·6 |
| 45 | 0·1 | 0·03 | 1·1 | 1·1 | 3·7 | 3·7 | 3·6 |
| 74 | 0·1 | 0·03 | 1·05 | 1·05 | 3·5 | 3·5 | |
| 64 | 0·1 | 0·14 | 4·3 | 4·3 | 3·1 | 3·1 | 3·0 |
| 75 | 0·1 | 0·14 | 4·0 | 4·0 | 2·9 | 2·9 | |

TABLE 7. *Effect of lithium nitrate on the radiometrically measured rate of mercury exchange ($k_0^{\text{Hg}}$ in mole l.$^{-1}$ sec.$^{-1}$), and on the second-order rate-constant of substitution ($k_2^{(3)}$ in mole$^{-1}$ l. sec.$^{-1}$) by s-butylmercuric nitrate (concentration a) in radiomercury-containing di-s-butylmercury (concentration b) in ethanol at* 0·0°.

| Runs | *a* (M) | *b* (M) | [LiNO$_3$] | $10^4k_0^{\text{Hg}}$ | $10^2k_2^{(3)}$ | Mean |
|---|---|---|---|---|---|---|
| All Tab. 6 | Various | Various | 0·0 | Various | 2·8—3·7 | 3·25 |
| 35, 39, 41 | 0·1 | 0·1 | 0·0 | 3·3—3·5 | 3·3—3·5 | 3·4 |
| 36 | 0·1 | 0·1 | 0·15 | 5·2 | 5·2 | 4·9 |
| 40 | 0·1 | 0·1 | 0·15 | 4·6 | 4·6 | |
| 42 | 0·1 | 0·1 | 0·15 | 4·8 | 4·8 | |

(5) *Mechanism of the Substitution.*—The reaction here considered has been identified as exemplifying the three-alkyl substitution (3), by double-labelling, and confirmatorily by kinetics, methods which exclude all other possible interpretations of the overall stoicheiometry. Three-alkyl substitution is a new reaction: the question of its mechanism therefore arises; and we shall consider the three electrophilic mechanisms of substitution, unimolecular $S_E1$, bimolecular $S_E2$, and internal $S_Ei$, preconceived in Part I.[2]

The complete retention of configuration in the substitution, and its second-order kinetic form, agree in excluding mechanism $S_E1$. But both results are consistent with either mechanism $S_E2$ or $S_Ei$. The rest of our kinetic investigation was designed to resolve this ambiguity; and again we can offer two separate pieces of evidence.

The question is essentially one of deciding whether an open or a cyclic formula best expresses the transition state of substitution, apart from its solvation. Our first method of attacking this problem is the same as one used in connexion with the two-alkyl substitution treated in Part II,[1] *viz.*, to examine the effect on rate of increasing the ionicity of the substituting agent, or, what comes to the same, making its potential or actual anion successively less prone to combine with the mercury atom which is being expelled. We find that the rate of substitution increases along the reagent-series, $\mathrm{Bu^sHgBr} <$ $\mathrm{Bu^sHg{\cdot}OAc} \ll \mathrm{Bu^sHg{\cdot}NO_3}$, where the single inequality sign expresses one power of ten, and the double one at least two powers. Such an increase of rate with ionicity is clearly more consistent with mechanism $S_E2$ than with mechanism $S_Ei$.

To provide confirmatory evidence, we studied kinetic salt effects on the substitutions using the extreme members of our reagent series, s-butylmercuric bromide and s-butylmercuric nitrate. It is useful to recall what happened in the similar study, in Part II,[1] of the two-alkyl reaction: the striking result was a strong specific retardation by lithium bromide of the reaction of mercuric bromide with di-s-butylmercury, according to a kinetic form which showed clearly that bromide ion was combining fairly firmly with mercuric bromide to form the complex anion, $HgBr_3^-$, the mercury atom in which was practically put out of action as an electrophilic substituting agent in this reaction. In the present study of salt effects on the three-alkyl reactions, the general result was that lithium salts weakly or moderately accelerate them, and that lithium bromide, in its effect on the reaction of s-butylmercuric bromide with di-s-butylmercury, is no exception. This shows, first, that bromide ion does not combine with alkylmercuric bromides to form complex anions $RHgBr_2^-$ nearly as firmly as it combines with mercuric bromide to form $HgBr_3^-$. We may also conclude from the general result that the transition states of the three-alkyl substitutions are more polar than their initial states; and that this is as true when the reagent is s-butylmercuric bromide as when it is s-butylmercuric nitrate; for the accelerating effects of the same salt in these two reactions were practically identical.

The accelerating effect of different lithium salts on the same reaction, that of s-butylmercuric bromide, followed broadly the tendency to ionic dissociation of the lithium salts. The order of the accelerating effects was: $LiOAc < LiNO_3 < LiBr < LiClO_4$, with only a small difference between the last two members of this series. We must remember in this connexion that a bromide, although among the least ionised of mercuric salts, and in this regard very different from the perchlorate,* is among the most ionically dissociated of lithium salts, and in this respect is comparable to the perchlorate. Indeed, as we know that, at least in acetone at greater dilutions than we here use, lithium bromide is more fully dissociated than the perchlorate,[9] we might have expected lithium bromide, if distinguishable from the perchlorate in its salt effect, to stand on the other side of it in our salt series. We would hesitate to speculate on the cause of this minor anomaly were there not further reason in the following papers for our interpretation, which is that bromide ion does have an appreciable affinity for alkylmercuric bromides, though not nearly so strong a one as for mercuric bromide; and that its association with s-butylmercuric bromide lowers the activity of that substance as an electrophilic reagent. In other words, we suggest that lithium bromide, in addition to its accelerating general salt effect, has a more weakly retarding specific effect on the three-alkyl substitution. The balance is the opposite of that obtaining in the two-alkyl substitution: there, the general effect of lithium bromide cannot be seen, because its specific effect is so powerful.

The above is only the fitting of a detail into the broad picture of the salt effects. This discloses a transition state of three-alkyl substitution, which is of similar form throughout the series of reactions studied, is a highly polar transition state, and is therefore probably an open one, apart from solvation, consistently with mechanism $S_E2$.

In the light of all our optical and kinetic evidence, our conclusion, in summary, is that, in the reactions of s-butylmercuric bromide, acetate, and nitrate, severally, with di-s-butylmercury in ethanol, the mercury-for-mercury replacement is a three-alkyl substitution, having the bimolecular electrophilic mechanism, $S_E2$, in which stereochemical

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* Presumably the unshared valency electrons of iodine (5*p*), bromine (4*p*), and, though more mildly, chlorine (3*p*), in mercuric salts, can conjugate effectively with the empty orbitals (6*p*) of the valency shell of mercury (+*T*-effect), whereas those of fluorine (2*p*), as of oxy-anions (2*p*), are too close to their nuclei to do so (and in oxy-anions are otherwise delocalised). However, orbital size-adjustment must be an important factor in the conjugation of the higher halogens.

[9] Dippy, Jenkins, and Page, *J.*, 1939, 1386; Evans and Sugden, *J.*, 1949, 270; Accascina and Schiavo, *Ann. Chim.* (*Italy*), 1953, **43**, 695; A. J. Parker, personal communication.

configuration is fully preserved. Thus, the three-alkyl substitution appears to be closely analogous in mechanism to the two-alkyl substitution,† on which we reported in Part II.[1]

## EXPERIMENTAL

(6a) *Materials.*—Most of the racemic or optically active s-butylmercuric salts, and the di-s-butylmercury, required for this work were prepared as described in Parts I and II,[2,1] and the following notes are supplementary. The preparation of s-butylmercuric nitrate was greatly improved by adding the nitric acid to the s-butylmercuric hydroxide under cooling with ice–salt, the internal temperature being close to 0°, and crystallising the initially obtained pink solid from ether–pentane between 20° and $-80°$; a good yield of colourless crystals, m. p. 51°, was obtained. *s-Butylmercuric acetate*, not described before, was prepared by reaction of di-s-butylmercury (10 g.) with mercuric acetate (10 g.) in methanol (100 ml.). After being kept overnight, the solution was filtered and evaporated under reduced pressure, the oily residue was taken up in ether, and the filtered extract was evaporated at room temperature. The solid residue was crystallised three times from pentane between 20° and $-80°$, whereupon its m. p. 29° became constant (Found: C, 22·4; H, 3·7. $C_6H_{12}HgO_2$ requires C, 22·7; H, 3·8%). Radioactive materials were prepared, starting from pile-irradiated mercuric oxide, after the short-lived isotopes (half-lives of the order of a day or less) had disappeared, and only $^{203}$Hg (half-life 46·5 days) and stable isotopes remained. This material, after dilution with inactive mercuric oxide, was converted by hydrobromic acid into radiomercuric bromide, which, after further dilution with mercuric bromide, was crystallised from ethanol. The product, on reaction with di-s-butylmercury, under conditions given by the kinetic investigation of Part II, produced s-butylradiomercuric bromide. Some of this product was converted by the Grignard method (cf. Part II) into di-s-butylradiomercury. Optically active s-butylradiomercuric bromide was made by the reaction of radiomercuric bromide, in the presence of lithium bromide, with optically active di-s-butylmercury (Part II), under conditions given by the kinetic investigation of Part V (accompanying). All these organic mercury compounds were stored in the dark at $-80°$.

(6b) *Polarimetric Kinetics with s-Butylmercuric Bromide.*—The optically active s-butylmercuric bromide was crystallised from pentane, and the racemic di-s-butylmercury was distilled under reduced pressure, just before use. The ethanol was dried by the method employing ethyl phthalate. After its optical rotation had been checked, weighed s-butylmercuric bromide was dissolved in most of the required ethanol at 35°, weighed di-s-butylmercury was added, and the volume was adjusted. Initially, and after known times at 35·0°, samples of 25 ml. were withdrawn, each to be run into an empty tube immersed in solid carbon dioxide–acetone. The precipitated s-butylmercuric bromide was collected and washed with pentane, and its specific rotation ($c = 5$, in acetone) was determined. Runs in which lithium salts were initially added were sampled in the same way, except that the recovered s-butylmercuric bromide was washed with water, and, when dry, with pentane. These procedures were shown to be correct by the check that the specific rotation of s-butylmercuric bromide thus recovered from the initially withdrawn sample was identical with that of the material used to make up the reaction solution. Rates of exchange, and rate-constants of substitution, determined in this way, are in Tables 1, 2, and 4. The course of an individual run is shown in Table 8.

(6c) *Radiometric Kinetics with s-Butylmercuric Bromide.*—In some runs s-butylradiomercuric bromide was used with non-radioactive di-s-butylmercury, and in others inactive

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† Dessy and Lee[10] have recently proposed a mechanism of $S_Ei$-type for the two-alkyl substitution, on the basis of their study of the rates of reaction of mercuric iodide with several dialkyl- and diarylmercurys in dry or aqueous dioxan. They embrace both the aliphatic and aromatic electrophilic substitutions in a single mechanism, though $\pi$-electrons might be expected to play a rôle in the aromatic substitutions. Their sharpest, indeed, their only sharp piece of evidence rests on their statement, unsupported by comparative figures, that the rate of reaction of mercuric iodide with diphenylmercury is unaffected by added lithium iodide. Since we know from the work of our Part II[1] that the reaction of mercuric bromide with di-s-butylmercury is strongly retarded by lithium bromide, their observation, if confirmed, would argue against a common aliphatic-cum-aromatic mechanism. However, the measurements were by light-absorption of mercuric iodide, and the experiment with added lithium iodide is not detailed, though these two salts would be expected to combine enough to change the absorption spectrum.

[10] Dessy and Lee, *J. Amer. Chem. Soc.*, 1960, **89**, 689.

s-butylmercuric bromide with di-s-butylradiomercury. In either case, s-butylradiomercuric bromide was isolated from timed samples of 25 ml. according to the procedure of Section 6b. The radiation counts were taken on 10 ml. of a solution of this substance in acetone in concentrations (not above 0·1M) and over periods (not above 1 hr.) adjusted according to the activity. Counts were corrected for background, and allowance was made for the slow decay of $^{203}$Hg by re-counting the initial sample on the day of the counting of any timed sample. Rates of exchange, and rate-constants of substitution, measured thus, are in Tables 2, 3, and 4. The course of an individual run is shown in Table 9.

(6d) *Radiometric Kinetics with s-Butylmercuric Acetate.*—These runs were followed by using non-radioactive s-butylmercuric acetate and di-s-butylradiomercury in ethanol at 35·0°.

TABLE 8. (*Run* 3) *Polarimetric rate of exchange* ($k_0^{\text{Alk}}$ *in mole l.*$^{-1}$ *sec.*$^{-1}$) *and second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *of optically active s-butylmercuric bromide and racemic di-s-butylmercury in ethanol at* 35·0°.

([Bu$^s$HgBr] = 0·1M; [Bu$^s_2$Hg] = 0·1M; $[\alpha]_D^{20}$ for $c = 5$, in acetone; $f = (3[\alpha_t] - [\alpha_0])/2[\alpha_0]$; $k_l = -(1/t)\ln f$; $k_0^{\text{Alk}} = 0{\cdot}2k_1/3$; $k_2^{(3)} = 100k_0^{\text{Alk}}$).

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $t$ (hr.) ............... | 0·0 | 19·0 | 24·0 | 29·0 | 43·0 | 49·0 | 69·5 | 116·5 | 504 |
| $[\alpha_t]_D^{20}$ ............... | −12·15° | −8·93 | −8·57 | −7·98 | −6·76 | −6·41 | −5·23 | −4·42 | −3·95 |
| $100\ (1 - f)$ ......... | 0·0 | 39·8 | 44·2 | 51·6 | 66·6 | 70·9 | 85·6 | 95·5 | 101 |
| $10^6k_1$ (sec.$^{-1}$) ...... | — | 7·41 | 6·74 | 6·96 | 7·06 | 6·99 | 7·72 | 7·17 | — |
| $10^7k_0^{\text{Alk}} = 10^5k_2^{(3)}$ | — | 4·94 | 4·49 | 4·62 | 4·71 | 4·66 | 5·15 | 4·78 | — |

TABLE 9. (*Run* 55) *Radiometric rates of exchange* ($k_0^{\text{Hg}}$ *in mole l.*$^{-1}$ *sec.*$^{-1}$) *and second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *of s-butylradiomercuric bromide with inactive di-s-butylmercury in the presence of lithium acetate in ethanol at* 35·0°.

([Bu$^s$HgBr] = 0·1, [Bu$^s_2$Hg] = 0·1, [LiOAc] = 0·1M; corrected count, $c$; $f = (2c_t - c_0)/c_0$; $k_1 = -(1/t)\ln f$; $k_0^{\text{Hg}} = 0{\cdot}1k_1/2$; $k_2^{(3)} = 100k_0^{\text{Hg}}$.)

| $t$ (hr.) | $c_t$ | $100\ (1 - f)$ | $10^6k_1$ (sec.$^{-1}$) | $10^7k_0^{\text{Hg}} = 10^5k_2^{(3)}$ |
|---|---|---|---|---|
| 0·0 | 7674 | 0·0 | — | — |
| 14·0 | 6028 | 44·6 | 11·7 | 5·8 |
| 18·0 | 5741 | 52·1 | 11·4 | 5·7 |
| 22·0 | 5483 | 58·8 | 11·2 | 5·6 |
| 26·0 | 5162 | 67·2 | 11·9 | 5·8 |
| 39·0 | 4727 | 78·2 | 10·9 | 5·4 |

Timed samples of 25 ml. were run into empty tubes immersed in solid carbon dioxide–acetone, and, to each, 10 ml. of 10% aqueous potassium bromide were added to precipitate s-butylradiomercuric bromide, which was collected and washed with water and, when dry, with pentane. Its radioactivity was measured as described in Section 6c. The rate-constants are in Table 5, and a specimen run is recorded in Table 10.

TABLE 10. (*Run* 81) *Radiometric rate of exchange* ($k_0^{\text{Hg}}$ *in mole l.*$^{-1}$ *sec.*$^{-1}$) *and second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *of s-butylmercuric acetate with di-s-butylradiomercury in ethanol at* 35·0°.

([Bu$^s$Hg·OAc] = 0·1M; [Bu$^s_2$Hg] = 0·1M; formulæ as in Table 9, except that $f = (c_\infty - c_t)/c_\infty$ with $c_\infty$ = half the count of initially used Bu$^s_2$Hg.)

| $t$ (hr.) | $c_t$ | $100\ (1 - f)$ | $10^6k_1$ (sec.$^{-1}$) | $10^7k_0 = 10^5k_3^{(3)}$ |
|---|---|---|---|---|
| 1·0 | 1583 | 18·1 | 55·5 | 27·7 |
| 2·5 | 3382 | 38·8 | 54·5 | 27·2 |
| 4·0 | 4564 | 52·2 | 51·4 | 25·7 |
| 6·0 | 5980 | 68·5 | 53·5 | 26·8 |
| ∞ | 8740 | 100 | — | — |

(6e) *Radiometric Kinetics with s-Butylmercuric Nitrate.*—The exchange between non-radioactive s-butylmercuric nitrate and di-s-butylradiomercury was too fast to measure at 35°, but was followed at 0° with the aid of a rapid-sampling technique. At a known time, about 25 ml. (not measured) of the solution were poured directly from the reaction flask into an empty tube cooled in liquid nitrogen. This quenching procedure was tested and shown to be adequate. Samples were thus quenched every 20—40 sec., depending on the rate, over periods between

1 and 4 min. They rapidly solidified and were afterwards placed for some hours in a bath of solid carbon dioxide–acetone, where they re-melted and deposited crystalline s-butylmercuric nitrate. The mother-liquor was decanted from each such sample of this salt, to which, after it had been washed with cooled ethanol by decantation, a few ml. of dioxan, then a calculated excess of 60% aqueous hydrobromic acid, and then water, were added. The s-butylradiomercuric bromide, which crystallised, was collected, and its radioactivity was measured as described in sections 6d and 6c. The rate-constants, calculated from four-point runs, such as that in Table 10, and by the same formulæ, are in Tables 6 and 7.

## APPENDIX

(7) *Rate Equations.*—First consider the chemical equation (4) (p. 1122) as if written reversibly. If $a$ and $b$ are the concentrations of alkylmercuric salt and dialkylmercury, respectively, and $x$ is the concentration of labelled mercury, originally in one of them, which has become transferred to the other at time $t$, then, because the rate-constant for bimolecular three-alkyl substitution $k_2^{(3)}$ must be the same for both directions, the rate of label-transfer will be

$$\mathrm{d}x/\mathrm{d}t = k_2^{(3)}\{(a - x)(b - x) - x^2\} = k_2^{(3)}\{ab - (a + b)x\} \quad . \quad . \quad . \quad . \tag{i}$$

At infinite time, $\mathrm{d}x/\mathrm{d}t = 0$, and hence $x_\infty = ab/(a + b)$. At zero time, $x = 0$, and hence

$$k_0^{\mathrm{Hg}} = (\mathrm{d}x/\mathrm{d}t)_0 = k_2^{(3)}ab \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{ii}$$

where $k_2^{(3)}$ is to be calculated from the integrated form of (i), which is

$$k_2^{(3)} = k_1/(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{iii}$$

$$k_1 = -(1/t)\ln f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{iv}$$

$$f = (x_\infty - x)/x_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{v}$$

Now consider the chemical equations (6) (p. 1123) as if written reversibly. Let $k_2^{(2)}$ be the rate-constant of formation of mercuric bromide by bimolecular two-alkyl substitution, and $k_2^{(-2)}$ the much larger rate-constant for the reverse of this reaction. An unlabelled molecule of mercuric bromide can be formed either from two unlabelled molecules of the alkylmercuric bromide, or from one labelled and one unlabelled; and a labelled mercuric bromide molecule can be formed either from the latter combination or from two labelled molecules. The mercuric bromide molecule produced in each of these four ways can react with either labelled or unlabelled dialkylmercury, to produce, in the one case, a pair of molecules like those it came from, and, in the other, an alternative pair containing a transferred label. Thus of the eight reaction sequences which form and destroy mercuric bromide, four lead to label-transfer. Consider one of these four. Two unlabelled alkylmercuric bromide molecules will produce unlabelled mercuric bromide at a rate $k_2^{(2)}\ (a - x)^2$, and a fraction $(b - x)/b$ of this product will react with the labelled dialkylmercury to give label-transfer at a rate $k_2^{(2)}(a - x)^2(b - x)/b$. Adding in the other three contributions to the rate of transfer, taking due account of direction, we find

$$\begin{aligned}\mathrm{d}x/\mathrm{d}t &= (k_2^{(2)}/b)\{(a - x)^2(b - x) + (a - x)(b - x)x - (a - x)x^2 - x^3\} \\ &= k_2^{(2)}(a/b)\{ab - (a + b)x\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .\end{aligned} \tag{vi}$$

At zero time, $x = 0$, and hence

$$k_0^{\mathrm{Hg}} = (\mathrm{d}x/\mathrm{d}t)_0 = k_2^{(2)}a^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{vii}$$

where $k_2^{(2)}$ is to be calculated from the integrated form of (vi). This is

$$k_2^{(2)} = k_1 b/a(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{viii}$$

where $k_1$ is given by equations (iv) and (v).

From either (ii) and (iv), or (vii) and (iv),

$$k_0^{\mathrm{Hg}} = k_1 ab/(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{ix}$$

Hence $k_0$ can be determined without assumptions as to which mechanism is responsible for exchange, and then the validity of the mechanism-dependent equations (ii) and (vii) can be tested, as in Section 4. This analysis is given for a mercury label. It is the same for an alkyl label, except that various factors of 2 and ½ enter into the working, which compensate. A similar derivation can be given of the relations between the unimolecular substitution constant $k_1^{(3)}$, and the exchange and label-transfer constants, $k_0^{\mathrm{Hg}}$ and $k_1$. All these relations are used in Sections 4 and 6.

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