Irradiation of 1-Methoxycycloheptatriene in the Presence and Absence of Oxygen. A solution of 1-methoxycycloheptatriene (500 mg) in oxygen-free benzene (250 ml) was irradiated with a Pyrex-jacketed Hanovia immersion lamp (Type A) for 1 hr. A 50-ml aliquot of this solution was taken, and the solvent was removed. Examination of the residual oil by nmr showed Ia (21%), VIa (55%), and IIa (24%).

The same scale experiment was repeated using oxygen-saturated benzene (oxygen was bubbled through the solution throughout the period of irradiation). After 1-hr irradiation, nmr analysis showed Ia (19%), VIa (59%), and IIa (22%).

Irradiation of 7-Methoxycycloheptatriene in the Presence and Absence of Acetophenone. A solution of 100 mg (0.0082 mole) of 7-methoxycycloheptatriene in 5 ml of oxygen-free benzene was prepared. This solution (1 ml) was placed in each of two Pyrex nmr tubes. To one of the tubes 30 mg of acetophenone was added, then both were sealed. The tubes were irradiated with a Pyrex-jacketed Hanovia immersion lamp (Type A) through a 2-mm-thick layer of filter solution (described above). At appropriate intervals the tubes were removed, and the nmr spectra were run. After 12-hr irradiation no significant reaction had occurred in either tube.

Irradiation of 1-Methoxycycloheptatriene in the Presence and Absence of Sensitizers. These irradiations were carried out using nmr tubes as described above. However, in this case, after 1-hr irradiation *ca.* 50% of the 1-methoxycycloheptatriene had rearranged to a mixture of 7-methoxycycloheptatriene and 1-methoxybicyclo[3.2.0]hepta-3,6-diene. Addition of 1 molar equiv of acetophenone definitely slowed down the rearrangement while a 10 molar equiv excess of acetophenone effectively halted the rearrangement as did 1 equiv of benzophenone. At the concentrations used (0.16 *M* in substrate and sensitizer) 1-methoxycycloheptatriene (ϵ_{3600} 4.1) had a slightly higher absorbance (0.65 at 3600 A) than acetophenone [ϵ_{3600} 3.1; *A* (0.16 *M*) = 0.49]. Using 0.16 *M* 1-methoxycycloheptatriene and 1.6 *M* acetophenone, the respective absorbances were 0.65 and 4.90. In this case >88% of the incident light is absorbed by the acetophenone. No reaction could be detected after 1-hr irradiation. Benzene absorption is not a problem (ϵ_{3400} 4.44×10^{-4}; $\epsilon_{3600} \approx 0$).

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The Mechanism of Isotopic Exchange between Arylmercuric Compounds and Elemental Mercury[1a]

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Abstract: The mechanism of the facile isotope exchange between arylmercuric compounds in solution and metallic mercury was examined. All reasonable mechanisms except a true isotopic exchange at the surface of the liquid are eliminated. The reaction rate is not significantly limited by mass transport in either phase. The reaction shows a real but small solvent dependence which is not correlated with the solubility of the substrate or any common solvent parameter. This and the value of $\Delta S^{\ddagger}$ favor a rate-determining chemisorbtion step. The efficiency of substrate collisions with the metal is much higher than that of collisions with the Hg^0 atoms in solution for bringing about exchange, suggesting a rate-determining electron transfer. Reactivity seems to be in the order RHgI > RHgBr > RHgCl > RHgOAc >> RHgR. An over-all mechanism is proposed.

Several years ago Reutov and Ostapchuk[2] reported that the isotope exchange shown in eq 1, rather surprisingly, proceeded under mild conditions in a variety of solvents. Halogen atoms, aryl groups, and

$$R_1HgR_2 + {}^{203}Hg^0 \rightleftharpoons R_1{}^{203}HgR_2 + Hg^0 \qquad (1)$$

certain special alkyl groups can be used as R_1 and R_2.[2–5] The original report has been confirmed and extended in a series of papers by Reutov and his co-workers,[3] and by Pollard and Westwood.[4,5] The most important findings of these workers have been that the reaction could be carried out under conditions where its rate was not transport controlled, and that it was totally unaccompanied by chemical changes. In the case that R_1 or R_2 is optically active there is not even a loss of optical activity accompanying the exchange.[3] From these observations, and others, a mechanism involving a four-center transition state was deduced.

The present paper describes the exchange between *p*-methoxyphenylmercurials, RHgX, and elemental mercury. In contrast with previous work the rate of encounter of the substrate with the surface can be estimated. The surface area and conditions were more closely controllable than those of previous investigators. A much wider range of substrate concentrations was conveniently studied by labeling the organomercurial rather than the elemental mercury. The effect of solvent on reactivity and the solubility of the substrate in the same solvents were extensively studied. The effect of varying X, through the halogens and acetate, was studied. An upper limit was placed on the rate of the analogous reaction in homogeneous solution. The findings that the exchange is interfacial, largely unlimited by mass transport, and unaccompanied by chemical reactions were confirmed. Surface encounters are at least several orders of magnitude more effective than encounters with mercury atoms in solution for producing exchange. This finding, com-

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(1) (a) Supported, in part, by the Petroleum Research Foundation through Grant PRF 1912-A3,4; (b) Sloan Foundation Fellow, 1960–1964; (c) Du Pont Teaching Assistant Awardee, 1963–1964; American Oil Foundation Fellow, 1964–1965; Shell Oil Co. Summer Fellow, 1963; National Science Foundation Summer Fellow, 1964; Du Pont Summer Fellow, 1966.

(2) O. A. Reutov and G. M. Ostapchuk, *Dokl. Akad. Nauk SSSR*, **117**, 826 (1957).

(3) O. A. Reutov, *Angew. Chem.*, **72**, 198 (1960); other papers by Reutov and his co-workers are referred to here.

(4) D. R. Pollard and J. V. Westwood, *J. Am. Chem. Soc.*, **87**, 2809 (1965).

(5) D. R. Pollard and J. V. Westwood, *ibid.*, **88**, 1404 (1966).

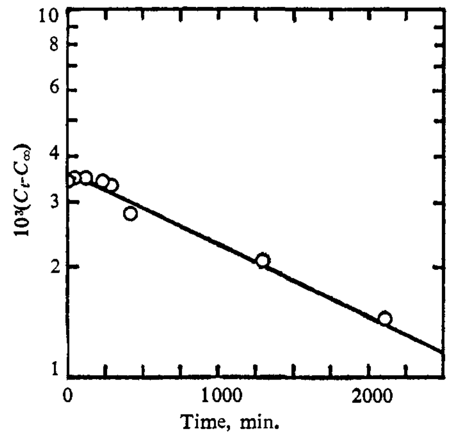

Figure 1. A typical plot of log ($C_t - C_\infty$) as a function of t for a homogeneous reaction; (RHgBr) was 1.38×10^{-5} M, and (Hg^0) was 0.99×10^{-5} M.

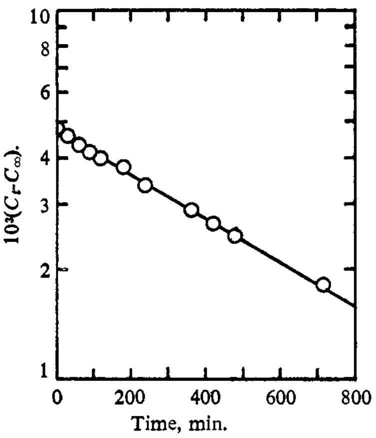

Figure 2. A typical plot of log ($C_t - C_\infty$) as a function of t for a heterogeneous reaction; (RHgBr) was 4.35×10^{-5} M, and 25.0 g of Hg^0 was used, giving a surface area of 2.0 cm.^{2} The temperature was 25°.

bined with the other findings, suggests that electron transfer from the substrate to the metal is rate determining for the exchange.

Results

It can be shown[6] that an isotopic exchange reaction in which a given element is exchanged between two different chemical environments follows the rate law shown in eq 2 within any given experiment regardless of the mechanism of the exchange. In eq 2 k is the

$$k = \frac{ab}{a+b}\,\frac{2.303}{t-t_0}\log\left(\frac{C_0 - C_\infty}{C_t - C_\infty}\right) \qquad (2)$$

constant rate of exchange of labeled atoms between the two environments, with units of M sec^{-1}; a and b are the concentrations of labeled substances in the two environments; t_0 is the time at which exchange was begun; t, the time at which it was interrupted; C_t is the counting rate at time t. Equation 2 is applicable to heterogeneous as well as homogeneous exchange reactions as long as the labeled atom does not accumulate significantly in the interfacial region. The disappearance of radioactivity from the labeled starting material was accurately described by eq 2, within the precision of the measurements, except where otherwise noted. Rate constants, k, were obtained by inspection from linear plots of log ($C_t - C_\infty$) as a function of time. Typical examples of such plots, for homogeneous and heterogeneous reactions, are shown in Figures 1 and 2.

Equation 2 is limited to exchange reactions which are unaccompanied by any net chemical change. The absence of such change was verified, in the present system, for a 5.4×10^{-5} M solution of RHgBr in methanol, exchanging with a 25-g sample of liquid mercury (2.0-cm^2 surface area). The ultraviolet spectrum of the RHgBr solution was not detectably diminished during ten half-lives of exchange. About 2% diminution would have been clearly detectable.

Homogeneous Solution. Four rates were measured at 25° in homogeneous benzene solution, with initially labeled RHgBr, using analytical reagent grade benzene. (The solubility of mercury in benzene is 1.2×10^{-5} M at 25°.[7]) The half-lives were about 2 days. The resultant k values are shown in Table I. The data are too scanty and imprecise to permit the establishment of a kinetic order with respect to either reagent, but if the reaction is *assumed* to be first order in each reagent the second-order rate constants, k_2, shown in Table I are obtained. Their average is 0.25 ± 0.05 M^{-1} sec^{-1}.

Table I. Rate of Exchange in Homogeneous Benzene Solution

(RHgBr), 10^5 M	(Hg^0), 10^5 M	10^9k, M^{-1} sec^{-1}	k_2, M^{-1} sec^{-1}
0.69	0.69	1.3	0.27
0.69	0.82	0.8	0.15
1.03	0.82	2.2	0.27
1.38	0.99	4.4	0.33

Some of the scatter may be due to catalysis by impurities. When the same reaction was carried out in a poorer grade of solvent k was larger by a factor of about 5 at comparable concentrations. If the kinetic order is incorrect, then the true, bimolecular, rate constant would be smaller yet. For these reasons, the value of k_2 given is more likely too large than too small.

Work on homogeneous solutions was not carried further because of the long half-lives and experimental difficulties involved.

Heterogeneous Exchange. Heterogeneous exchange experiments were carried out in a round-bottomed flask with a mechanical stirrer and openings for the addition and withdrawal of materials. It is identical with that previously described,[8] except that it had an indentation in the bottom of the flask to help stabilize the mercury sample and a piece of speedometer cable between the stirring motor and the stirrer to reduce vibration of the flask. This apparatus does not break up the mercury sample at the stirrer speeds used.

In the heterogeneous experiments the concentration of mercury in liquid mercury (68 g-atoms l.$^{-1}$) is higher by a factor of 10^5 than the highest solution concentration used, and the quantity of mercury in the liquid is

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(6) O. Meyers and R. J. Prestwood in "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, pp 9 and 34.

(7) E. H. Klehr, Ph.D. Thesis, Iowa State University, 1959.

(8) P. Warrick, Jr., E. M. Wewerka, and M. M. Kreevoy, *J. Am. Chem. Soc.*, **85**, 1909 (1963).

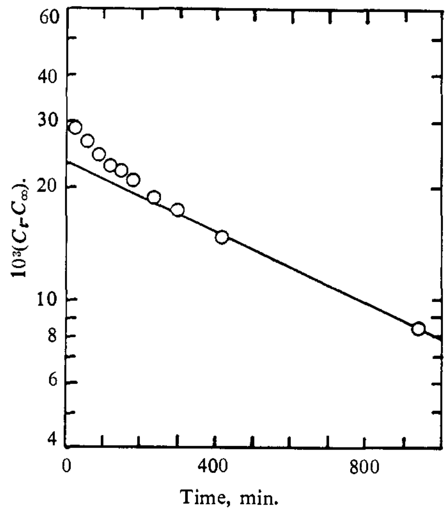

Figure 3. Typical curved plot of log $(C_t - C_\infty)$ as a function of t at low (RHgBr). The (RHgBr) was 6.93 × 10^{-6} M in benzene; 25 g of Hg^0 was used (2.0-cm^2 surface area) at 600 rpm and 25°. The solid line corresponds to a k_1 of 1.8 × 10^{-5} sec^{-1}.

higher by a factor of 10^3 than that in solution, so eq 2 reduces to eq 3, in which a is the concentration of

$$k/a = 2.303/(t - t_0) \log (C_0/C_t) \qquad (3)$$

RHgX.

Order With Respect to RHgBr. A series of experiments was carried out with varying concentrations of RHgBr in benzene, 25.0-g samples of Hg^0 (giving a 2.0-cm^2 surface area) at 25° and a stirring rate of 600 rpm. These were designed to test the reproducibility of the results and determine the order with respect to RHgBr. The results are shown in Table II. On repetition of an experiment without altering the apparatus reproducibility of better than 10% could usually be obtained. However, if the apparatus was disassembled and reassembled on another day, a discrepancy of almost a factor of 2 could sometimes be observed. This is exemplified by the results at 3.31 × 10^{-4} M RHgBr and 3.82 × 10^{-4} M RHgBr. Vibration of the apparatus is probably the cause of this variability. Reaction was notably faster when the apparatus was visibly vibrating. Within these limits the results in Table II are consistent with first-order behavior, and with no other simple order. The first-order rate constants, k_1, given by k/a, may show a slight, systematic, trend toward higher values at lower (RHgBr). Disregarding any drift, the average value of k_1 was 1.6 × 10^{-5} sec^{-1} with an average deviation from the mean of 0.4 × 10^{-5} sec^{-1}.

At (RHgBr) < 2 × 10^{-5} M curvature was increasingly apparent in plots of log $(C_t - C_\infty)$ as a function of t. Such a plot is shown in Figure 3. The origin of the curvature is not known, but it is probably associated with the loss of a small quantity of RHgBr from solution, significant by comparison with the very small quantities initially involved. The *terminal* slope of such plots gave k_1 values consistent with those obtained at higher (RHgBr). The beginning of such curvature, unnoticeable at slightly higher (RHgBr), is probably responsible for the slight drift to higher values of k_1 at lower (RHgBr) in Table II.

Table II. Exchange of RHgBr in Benzene Solution with 25 g of Hg^0 at 25°

(RHgBr), 10^5 M	$10^{10}k$, M^{-1} sec^{-1}	$10^5k/a$, sec^{-1}	k/a^2, M^{-1} sec^{-1}
1.7	3.4	2.0	1.2
2.0	3.8	1.9	0.95
2.7^a	4.3^a	1.6^a	0.59^a
4.2^b	9.7^b	2.3^b	0.55
4.4	10.1	2.3	0.52
5.1	7.6	1.5	0.29
9.3	13.0	1.4	0.15
10.9	14.2	1.3	0.12
15.6	15.6	1.0	0.06
18.6	20	1.1	0.06
26.2	26	1.0	0.04
33.1	46	1.4	0.04
38.2	31	0.8	0.02
66.1	93	1.4	0.02

[a] Four experiments, with average deviation from the mean, 2%. [b] Three experiments, with average deviation from the mean, 10%.

State of Aggregation of RHgBr. The method of differential vapor pressures[9] was used[10] to determine a van't Hoff i of 1.0 for RHgBr.

Mercury Surface Area. The rate was studied as a function of surface area, A, with RHgBr in benzene solution at 25°, at a stirring rate of 600 rpm. Except where noted, (RHgBr) was 4 × 10^{-5} M. The surface area was varied by varying the size of the mercury sample, and determined by measurement with calipers. In this way the surface area could be increased by a factor of more than 6. As shown in Table III, k_1/A is constant within the precision of the measurements. Variation of the sample size also changed the vertical distance between the stirrer and the mercury surface. It was independently shown that k_1 was invariant under comparable changes in the distance between the surface and the stirrer at constant mercury sample size and surface area. The 25-g sample, with 2.0-cm^2 surface area, was adopted as standard and used throughout the rest of this work. Rate constants per unit area can be obtained by dividing those reported by 2.0.

Table III. Variation of k_1 with Surface Area

A, cm^2	$10^6k_1/A$, sec^{-1} cm^{-2}
2.0	8.0^a
6.2	5.6
8.6	8.4
10.7	8.8
13.2	6.4

[a] Average of 20 determinations, taken from Table II.

Stirring Rate. The variation of k_1 with stirring rate was studied for RHgBr in several solvents at 25° with 25-g mercury samples and substrate concentrations around 4 × 10^{-5} M. The results are shown in Table IV for benzene. They were similar for isooctane (2,2,4-trimethylpentane) and nitrobenzene. There is no significant variation of reaction rate with stirring rate at or above 400 rpm.

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(9) S. Bruckenstein and A. Saito, *J. Am. Chem. Soc.*, **87**, 698 (1965).

(10) These measurements were kindly made for us by Mr. D. F. Untereker in consultation with Professor Bruckenstein.

Table IV. Variation of k_1 for RHgBr with Stirring Rate in Benzene at 25°

Stirring rate, rpm	10^5k_1, sec^{-1}
100	0.6
200	0.8
400	1.6
600	1.6[a]
800	1.7

[a] Average of 20 determinations, taken from Table II.

Medium and Ligand Effects. The variation in k_1 with solvent and with X, in RHgX, was studied at 25°, with 25-g mercury samples. In most systems several substrate concentrations were used, and first-order behavior verified. The results are shown in Table V.

Table V. Variation in Rate with Solvent and Ligand at 25°

	Substrate, 10^5k_1, sec^{-1}			
Solvent	RHgOAc	RHgCl	RHgBr	RHgI
$[(CH_3)_2N]_3PO$	0.21	0.24	0.21	0.24
$C_6H_5NO_2$			0.8	
$C_6H_5OCH_3$			1.0	
C_6H_6	0.16	0.41	1.6[a]	6.0
$C_6H_5CH_3$			1.7	
$(CH_3)_2CO$			1.9	
CH_3OH		1.5	2.9	
H_2O	3.7		4.4	
CCl_4			7.7	
Isooctane		6.4	9.8	10.5

[a] Average of 20 determinations, taken from Table II.

Effect of Temperature. In order to determine the thermodynamic parameters of activation, k_1 was measured for RHgBr in toluene, using a 25-g mercury sample and a 600 rpm stirring rate, at four temperatures between 1 and 40°. A total of seven determinations of k_1 were made. The logarithm of k_1/T was a linear function of $1/T$ within the precision of the measurements. Standard equations[11] were used to get the enthalpy of activation, $\Delta H^{\ddagger}$, by the method of least squares.[12] It had the value, 8.1 kcal mole^{-1}, with 50% confidence limits of 0.2 kcal mole^{-1} and 90% confidence limits of 0.6 kcal mole^{-1}.

The value of the entropy of activation, $\Delta S^{\ddagger}$, depends on the standard state chosen for the starting state and *for the transition state*. For ease of interpretation a 1 *M* ideal solution in toluene has been chosen for the starting state and *1 mole cm^{-2} for the transition state*. The smoothed value of k_1 at 25°, 1.75×10^{-5} sec^{-1}, must then be multiplied by the solution volume, 0.15 l., and divided by the reactive surface area, 2 cm^2, before $\Delta F^{\ddagger}$, the free energy of activation, can be obtained from eq 4.[11] In eq 4 k_r is the rate constant described

$$\Delta F^{\ddagger} = -RT \ln (k_r h/kT) \qquad (4)$$

above, with a value of 1.3×10^{-6} l. sec^{-1} cm^{-2} at 25° in toluene, and the other quantities are the usual physical constants. This leads to a value of 25.5 kcal mole^{-1} for $\Delta F^{\ddagger}$, and, *via* the usual thermodynamic equalities,[11] to a value of −58.4 cal mole^{-1} deg^{-1} for $\Delta S^{\ddagger}$, with 50% confidence limits of 0.7 cal mole^{-1} deg^{-1}.

Inhibition and Catalysis. A number of substances were tested for catalytic or inhibitory effects. For the most part these were substances known to or expected to adsorb on a mercury surface, or to complex the substrate. These experiments were carried out with RHgBr as the substrate, a 600-rpm stirring rate, and a 25-g mercury sample. In methanol as a solvent, 4×10^{-1} *M* sodium bromide and 1.4×10^{-1} *M* hydroquinone were without measureable effect. In benzene as a solvent, silicone grease and 6×10^{-4} *M p*-bromoanisole were without effect. However, 4×10^{-4} *M* stearic acid retarded the rate in benzene by a factor of about 2; 1.4×10^{-6} *M* $HgBr_2$ and also 2.6×10^{-6} *M* $HgBr_2$ accelerated it by about the same factor, both by comparison with a standard k_1 of 1.6×10^{-5} sec^{-1}. These changes appear to be outside of the scatter shown in Table II, although not far outside.

Reaction of $HgBr_2$ with Mercury. Mercuric bromide in solution reacts with liquid mercury, giving solid Hg_2Br_2. In isooctane, the ultraviolet spectrum of residual $HgBr_2$ can be detected, but no evidence of Hg_2Br_2 can be found in solution, so the equilibrium can be formulated as shown in eq 5. Using ^{203}Hg as a

$$HgBr_2(soln) + Hg^0(l) \rightleftharpoons Hg_2Br_2(s) \qquad (5)$$

tracer, and assuming that all the mercury in solution was in the form of $HgBr_2$, the equilibrium constant K_5 was measured for benzene solutions. Five determinations were made: two starting with solutions of $HgBr_2$, liquid mercury, and no Hg_2Br_2, and three starting with liquid mercury, freshly precipitated Hg_2Br_2, solvent, and no $HgBr_2$. The average value of K_5 was 2.5×10^5 M^{-1}, with an average deviation from the mean of 0.5×10^5 M^{-1}, and no systematic difference between those run forward and those run backward.

The experiments to test the catalytic effectiveness of $HgBr_2$ were carried out at concentrations well below the equilibrium concentration of $HgBr_2$, 4×10^{-6} *M*, so that no Hg_2Br_2 should have been present at equilibrium. Nevertheless, a few minutes after the reaction was begun, a precipitate of Hg_2Br_2 appeared at the metallic surface. After about 1 hr, the precipitate redissolved, so that, *at equilibrium*, the conditions of equilibrium were satisfied. The exchange reaction (eq 1) was proceeding all during the precipitation and resolution, but its rate was not detectably affected by these phenomena. This whole group of observations undoubtedly deserves, and will receive, further attention.

Disproportionation. An attempt was made to determine the equilibrium constant K_6 for the reaction shown in eq 6. It was determined (by spectrophotometry in the presence of 0.1 *M* NaI) that water in equilib-

$$2RHgBr \rightleftharpoons R_2Hg + HgBr_2 \qquad (6)$$

rium with 8.2×10^{-4} *M* RHgBr contained less than 10^{-6} *M* of $HgBr_2$. Since the distribution constant of $HgBr_2$ between water and benzene is 0.90 (favoring benzene)[13] an upper limit of 1.8×10^{-6} can be set for K_6.

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(11) M. M. Kreevoy in "Investigation of Rates and Mechanisms of Reactions," S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 1392.

(12) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 36–40.

(13) M. S. Sherrill, *Z. Physik. Chem.*, **43**, 705 (1903).

Solubility. The solubility, S, of RHgBr in all the solvents used for rate measurements was determined at 25°. Each measurement was made at least once from each direction, *i.e.*, by saturating an initially unsaturated solution with excess solid, and by allowing an initially supersaturated solution to equilibrate with the solid. The concentration of the equilibrated solutions was determined spectrophotometrically in methanol, by means of their radioactivity, using labeled RHgBr in the other solvents. Both methods were used for isooctane, and were in good agreement. The results are shown in Table VI.

Table VI. Solubility of RHgBr at 25°

Solvent	S, M
Water	1.4×10^{-5}
Isooctane	5.1×10^{-5} [a]
Isooctane	5.2×10^{-5} [b]
Methanol	2.3×10^{-3}
Toluene	3.5×10^{-3}
Benzene	5.6×10^{-3}
Hexamethylphosphoramide	6.2×10^{-3}
Anisole	8.9×10^{-3}
Nitrobenzene	1.8×10^{-2}
Acetone	1.9×10^{-2}

[a] Measured spectrophotometrically. [b] Measured by means of radioactivity.

In addition, 12 determinations of S in toluene were made at a series of temperatures between 0 and 55°. A plot of log S as a function of $1/T$ was linear, within the scatter of the measurements. From these data, using the van't Hoff equation[14] and the method of least squares,[12] the standard enthalpy of solution, $\Delta H°$, is 4.9 kcal mole^{-1}, with 50% confidence limits of ± 0.15 kcal mole^{-1}. Properly, this pertains to the midpoint of the temperature range studied, 27.5°. Using the standard equations, the entropy of solution, $\Delta S°$, is 5.1 ± 0.5 cal mole^{-1}, deg^{-1} if an ideal, 1 M, solution is chosen as standard state for RHgBr(soln) and the solid itself is the standard state for RHgBr(s).

Discussion

The present work supports the earlier conclusion[2-5] that the rate of the exchange reaction, eq 1, is not, generally, mass transport controlled. For the fastest exchanging compounds, in the most activating solvents, however, mass transport in the solution phase may play a role. For example, RHgI in isooctane exchanges with a rate constant almost half that for mercury reprecipitation under similar conditions[8] after correction for the difference in surface area. The latter reaction is thought to be mass transport controlled,[8] and it has been shown that the diffusion coefficient of atomic mercury in isooctane is not strikingly different from those of other species.[15] Most of the other exchange reactions were substantially slower than that of RHgI in isooctane, however, so the mass transport process must be relatively unimportant in determining their rates. This conclusion is supported by the substantial variation in exchange rate with substrate structure and by the invariance of the exchange rate with the stirring rate. In addition, $\Delta H^{\ddagger}$ for exchange in toluene is $\sim$5 kcal mole^{-1} larger than would be expected for a transport-controlled reaction.[16]

The diffusion of radioactive mercury away from the interface seems totally unimportant in determining the exchange rate. This is shown by the linear plots of log C_t as a function of t,[6] by the variation of rate as a function of X and solvent, and by a calculation of the concentration of labeled mercury at the interface during an exchange. In this calculation it was assumed that a concentration of labeled mercury atoms, C_{Hg^0}, was continuously maintained by the exchange at the surface of a cylindrical well of mercury. (This is the condition that would prevail if the exchange rate *were* controlled by diffusion in the mercury.) Standard equations[17] and the known self-diffusion coefficient of mercury[18] were then used to calculate the concentration of labeled mercury, C_{Hg}, as a function of C_{Hg^0} and the distance from the surface, at a time comparable to a half-life for exchange. The area under this curve was equated to the quantity of labeled mercury deposited from the most concentrated reaction mixture in a half-life. This gave a value for the only variable, C_{Hg^0}. It was 3×10^{-2} M, which can be compared with a total mercury concentration of 68 M in Hg^0(l).

An exchange mechanism involving HgX$_2$, shown in eq 7 and 8, has been discounted by Reutov.[3] The present results on disproportionation rigorously disallow it as the major exchange path.

$$2\mathrm{RHgX} \rightleftharpoons \mathrm{HgX_2} + \mathrm{R_2Hg} \tag{7}$$

$$\mathrm{HgX_2} + \mathrm{Hg^0(l)} \rightleftharpoons \mathrm{Hg_2X_2} \tag{8}$$

These set an upper limit of 10^{-6} M on the concentration of HgBr$_2$ in equilibrium with 8.2×10^{-4} M RHgBr in benzene at 25°. Assuming the mercury reprecipitation and the reaction shown in eq 8 are mass transport limited they would both have first-order rate constants of 3.2×10^{-4} sec^{-1}.[8] This leads to an exchange rate of 3.2×10^{-10} g-atom sec^{-1}, and an apparent first-order rate constant for RHgBr exchange of 4×10^{-7} sec^{-1}. This is only 2.5% of the observed rate constant under these conditions, 1.6×10^{-5} sec^{-1}. Even when the HgBr$_2$ concentration is increased by deliberate addition, the reactions shown in eq 7 and 8 cannot account for as much as 10% of the observed k_1, so they cannot even account for the apparent catalysis by added HgBr$_2$ Entirely similar reasoning excludes significant contributions to the overall exchange from the reactions shown in eq 9 and 10.

$$\mathrm{Hg^0(soln)} \rightleftharpoons \mathrm{Hg^0(l)} \tag{9}$$

$$\mathrm{RHg^*Br} + \mathrm{Hg^0(soln)} \rightleftharpoons \mathrm{RHgBr} + \mathrm{Hg^{0*}(soln)} \tag{10}$$

The foregoing excludes all of the reasonable mechanisms for exchange except those involving the direct interaction of RHgX with the surface. A generalized scheme for a surface mechanism is shown in eq 11-13.

$$\mathrm{RHg^*X(soln)} \rightleftharpoons \mathrm{RHg^*X(surf.)} \tag{11}$$

$$\mathrm{RHg^*X(surf.)} + \mathrm{Hg^0(l)} \rightleftharpoons \mathrm{RHg^*X \cdot Hg} \tag{12}$$

$$\mathrm{RHg^*X \cdot Hg} \rightleftharpoons \mathrm{RHgX \cdot Hg^*} \tag{13}$$

In those equations, RHg*X (surf.) represents unreacted

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(14) G. N. Lewis and M. Randall, "Thermodynamics", 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 173.

(15) M. M. Kreevoy and H. B. Scher, *J. Phys. Chem.*, **69**, 3814 (1965).

(16) L. L. Bircumshaw and A. C. Riddiford, *Quart. Rev.* (London), **6**, 157 (1952).

(17) J. Crank, "The Mathematics of Diffusion," Oxford at the Clarendon Press, London, 1956, p 18.

(18) D. S. Brown and D. G. Tuck, *Trans. Faraday Soc.*, **60**, 1230 (1964).

substrate in contact with the surface and $RHg^*X \cdot Hg$ represents chemisorbed but unexchanged substrate. If eq 13 represents the rate-determining step, k_1 is given by $k_{13} \times K_{12} \times K_{11}$, where k is a rate constant, K is an equilibrium constant, and the subscript gives the equation to which the constant pertains. There should be little solvent specificity for K_{11} and not very much for k_{13}, since it pertains to a reaction of a chemisorbed species, rather than one in solution. On the other hand, K_{12} should approximate inverse proportionality with S, since it pertains to a process that removes RHgBr from solution. This suggests that k_1 should show an approximate inverse proportionality with S. Comparison of Tables V and VI reveals little correlation between k_1 and S. Reutov and Ostapchuk[2] have indicated that the rate is independent of solvent. While the variation in k_1 with solvent is unquestionably real, it is considerably smaller than the variation in S. These observations make it unlikely that the reaction shown in eq 13 is rate determining. It has already been shown that mass transport, eq 11, is not rate determining. This leaves only the chemisorbtion step, eq 12, as an attractive rate-determining step. The present and previous[2-5] results are entirely compatible with this hypothesis provided that the transition state resembles the starting state.

The substituent effects on reactivity reported by Pollard and Westwood[5] indicate that the aromatic fragment becomes somewhat electron deficient in the transition state, but the effects are small. Pollard and Westwood report a Hammett ρ of -1 for substitution at *both* aryl groups. Values between 2 and 3 are commonly observed for generation of unit charge on an atom directly attached to the ring,[19] and since there are two substituted benzene rings in the present case, an even larger effect might be expected if unit charge were involved. The present results could be taken to indicate the development of an electron deficiency on mercury in the transition state, as the rate increases steadily with decreasing electronegativity. However, such a correlation would imply that di-*p*-anisylmercury (RHgR) should react faster than RHgI. In fact it has a rate constant which extrapolates to 3.6×10^{-10} l. cm^{-2} sec^{-1} at 25° in benzene.[5] This is slower by some 2.5 powers of 10 than RHgOAc and slower by a factor of 10^4 than RHgI. The observation that RHgR exchanges more slowly than RHgCl also seems to contradict the postulate[5] that the rate-determining step for exchange resembles that for electrophilic substitution. Electrophilic substitution by H^+ is much faster with diphenylmercury than with phenylmercuric chloride, so that the latter is the *product* of the reaction of diphenylmercury with dilute methanolic HCl.[20]

The *very* small changes accompanying changes in ligand and the slow reactions in hexamethylphosphoramide suggest complete ionization in that solvent, probably with the formation of ion pairs, $RHg(solvent)^+X^-$.

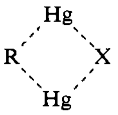
If the $\Delta S^{\neq}$ values reported by Pollard and Westwood[5] are recalculated for standard states of an ideal, 1 M solution for the starting state and 1 mole cm^{-2} for the transition state they give values (except for dibenzylmercury) quite close to that reported here. Diphenylmercury, for example, gives -57 cal $mole^{-1}$ deg^{-1}. (The original values appear to refer to a standard state of 1 mole/20 ml for the starting state and 1 mole/1000 cm^2 for the transition state.) Thus the differences in reactivity commented on above are probably due, in largest part, to changes in $\Delta H^{\neq}$.

If the changes in the entropy of solvation and the entropy of the metal accompanying the activation process can be neglected, the observed $\Delta S^{\neq}$ values are consistent with a transition state in which one translational degree of freedom has become the reaction coordinate. With standard states of 1 mole cm^{-3} for the starting state and 1 mole cm^{-2} for the transition state, the loss of one degree of translational freedom in the latter leads to the entropy shown in eq 14 for a

$$\Delta S^{\neq} = -R \ln (2\pi mkTe)^{1/2}/h \qquad (14)$$

gas.[21] The symbols have their usual significance. The value of $\Delta S^{\neq}$ computed is -41.6 cal $mole^{-1}$ deg^{-1}. The use of 1 M as the standard state for the starting material adds another $-R \ln 10^3$, so that the final calculated value is -55.3 cal $mole^{-1}$ deg^{-1}. The very good numerical agreement between this and the experimental value (-58.4 ± 0.7 cal $mole^{-1}$ deg^{-1}) is fortuitous. The calculated value would probably be 1–5 cal $mole^{-1}$ deg^{-1} smaller if a proper calculation could be made for the solution.[22] Nevertheless the agreement does strongly suggest that considerable translational freedom parallel to the surface is retained by the transition state. If this were lost, a much more negative value would be obtained (< -100 cal $mole^{-1}$ deg^{-1}).[21]

Previous workers[2-5] have favored a four-center, over-all transition state, **1**, for this reaction, without specifying whether this stage is reached during the chemisorbtion or subsequent steps. It now seems unlikely that **1** could be the over-all transition state for the reaction. The strongest argument against it is the relative efficiency of the surface reaction as compared to the homogeneous solution reaction. The simplest models[23] for collisions in solutions give collision rate constants



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[19] G. B. Barlin and D. D. Perrin, *Quart. Rev.* (London), **20**, 75 (1966).

[20] H. Zimmer and S. Makower, *Naturwissenschaften*, **23**, 551 (1954).

[21] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p 398.

[22] The translational entropy in solution is less than that in the gas phase by about 3 cal $mole^{-1}$ deg^{-1} for a molecule of about this molecular weight which does not interact specifically with the solvent. For example, the entropy of solution of I_2 vapor in isooctane is -3.2 cal $mole^{-1}$ deg^{-1} [J. H. Hildebrand and D. N. Glew, *J. Phys. Chem.*, **60**, 618 (1956)]. Thus, the loss of one degree of translational freedom for such a molecule would lead to an entropy contribution about 1 cal $mole^{-1}$ deg^{-1} less negative than a similar loss from the gas phase. However, the entropy of solution of RHgBr vapor in toluene would be more negative than that of I_2 in isooctane because its entropy of solution from the solid, 5 cal $mole^{-1}$ deg^{-1}, is less positive than the entropy of solution of solids which give noninteracting solutions. For example, naphthalene, biphenyl, and diphenylamine all give entropies of solution in benzene of 17–18 cal $mole^{-1}$ deg^{-1} [H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds," The Macmillan Co., New York, N. Y., 1963, pp 1434, 1436, and 1552; K. Suzuki and S. Seki, *Bull. Chem. Soc. Japan*, **28**, 417 (1955); G. Gehlhoff, *Z. Physik. Chem.*, **98**, 252 (1921)]. The exact effect of this on $\Delta S^{\neq}$ is impossible to evaluate but 5 cal $mole^{-1}$ deg^{-1} seems like a reasonable upper limit.

[23] E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford at the Clarendon Press, London, 1947, pp 8–9.

of 33 l. sec^{-1} cm^{-2} for a surface and $\sim 10^{11}$ M^{-1} sec^{-1} for bimolecular collisions in solution. The pertinent observed rate constants in benzene are 1.2×10^{-6} l. sec^{-1} cm^{-2} for the surface reaction and 0.25 M^{-1} sec^{-1} in solution, so the fraction of successful conversions in the former case is 4×10^{-8}, and, in the latter, 3×10^{-12}. More sophisticated treatment of the collision frequencies[24] may substantially alter these numerical values, but the conclusion that the surface reaction is much more efficient is not altered unless the substrate is attracted to the surface in strong preference to the solvent. Considering the solvent structures represented in Table V, this seems quite unlikely. It is hard to see why a transition state like **1** should be more easily formed from liquid mercury than from a mercury atom in solution. The former would seem to require most of the energy necessary to abstract a mercury atom from the liquid (8 kcal mole^{-1}) in addition to most of the energy required by the latter.

It is also hard to see how **1** could be compatible with the requirement that the transition state retains its mobility parallel to the surface, as suggested by $\Delta S^{\ddagger}$.

A rate-determining step that is consistent with all the evidence is electron transfer from the substrate to the mercury. This would account for the particular effectiveness of the metal, since its electron affinity must be essentially the same as its work function, 105 kcal mole^{-1},[25] while that of atomic mercury is 30–40 kcal mole^{-1}.[26] There is no definitive experimental evidence excluding **1** as a transition state for a fast exchange step following the chemisorbtion step, but there is also no evidence strongly supporting it. We prefer the mechanism shown in eq 15–18 because of its analogy with the reversible formation of the mercurous halides at a mercury surface. A definitive conclusion will

$$\mathrm{RHg^*X(soln)} + \mathrm{Hg^0(l)} \overset{\text{slow}}{\rightleftharpoons} \mathrm{Hg^-{\cdot}Hg^*RX^+(surf.)} \qquad (15)$$

$$\mathrm{Hg^-{\cdot}Hg^*RX^+(surf.)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{RHgHg^*X(surf.)} \qquad (16)$$

$$\mathrm{RHgHg^*X(surf.)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{XRHg^+{\cdot}Hg^{*-}(surf.)} \qquad (17)$$

$$\mathrm{XRHg^+{\cdot}Hg^{*-}(surf.)} \overset{\text{slow}}{\rightleftharpoons} \mathrm{RHgX(soln)} + \mathrm{Hg^{*0}\ (l)} \qquad (18)$$

have to depend on further experimental results.

Experimental Section

Materials. The general scheme by which the various radioactive mercury compounds were prepared is shown.

$$\begin{tikzcd}
\mathrm{RBr + Mg} \arrow[r, "\mathrm{THF}"] & \mathrm{RMgBr} \arrow[d, "\begin{array}{l}1.\ (C_4H_9O)_3B \\ 2.\ HCl{-}H_2O\end{array}"] & \\
& \mathrm{R_2BOH} \arrow[r, "\mathrm{Hg^*Br_2}"] \arrow[d, "\mathrm{Hg^*Cl_2}"] & \mathrm{RHg^*Br} \\
\mathrm{RHg^*I} & \mathrm{RHg^*Cl} \arrow[l, "\mathrm{KI}"'] \arrow[r, "\mathrm{AgOAc}"] & \mathrm{RHg^*OAc}
\end{tikzcd}$$

Bis(*p*-methoxyphenyl)borinic acid was prepared in 27% yield by the method of Hawthorne.[27] It had mp 102–105° (lit.[27] 107°).

The two *p*-methoxyphenylmercuric halides were prepared by the method of Torssell[28] from the borinic acid and the appropriate mercuric halide. The latter were labeled simply by mixing them in solution with small amounts of labeled $Hg(NO_3)_2$ in aqueous HNO_3, which is the form in which the ^{203}Hg was obtained. The labeled chloride was obtained in 95% yield and had mp 251.0–251.5°, in a sealed, evacuated capillary (lit.[28] 249–250°). The bromide was obtained in 44% yield and had mp 255–256°, in a sealed, evacuated capillary (lit.[28] 255–256°).

To obtain *p*-methoxyphenylmercuric acetate 0.31 g (9×10^{-4} mole) of the labeled chloride in 60 ml of hot benzene was treated with 0.14 g (8.5×10^{-4} mole) of silver acetate in 80 ml of ethanol (containing just enough water to give a clear solution). A precipitate formed immediately. The reaction mixture was refluxed gently for 15 min to coagulate the precipitate, which was then filtered. The solvent was removed from the filtrate under vacuum. The residual solid was recrystallized from ethyl acetate to give 0.18 g of product (4.9×10^{-4} mole, 54% yield), mp 179.5–180.5°, in a sealed, evacuated capillary (lit.[29] 178–179°).

To obtain the iodide, 0.52 g (1.5×10^{-3} mole) of the radioactive chloride was dissolved in 200 ml of benzene and shaken with four 25-ml portions of a 50% (by weight) solution of potassium iodide in water. The benzene layer was then separated and dried over magnesium sulfate. The solvent was removed under vacuum and the product recrystallized from 30 ml of ethyl acetate to give 0.30 g (0.7 mole, 45% yield) of labeled *p*-methoxyphenylmercuric iodide, mp 237–238° in a sealed, evacuated capillary (lit.[30] 237.8–238.1°).

The benzene, carbon tetrachloride, and isooctane used in kinetic and solubility studies were of spectrograde quality. The first two were obtained from Mallinckrodt Chemical Works, Inc., the latter from Phillips Petroleum Co. Hexamethylphosphoramide was obtained from Aldrich Chemical Co., and was their best grade. All of these were used without further purification. Methanol was obtained from E. I. duPont de Nemours, & Co., Inc., anisole from Aldrich Chemical Co., nitrobenzene, acetone, and toluene from Eastman Kodak Co., and all were purified by distillation. Triply distilled mercury was used.

Kinetic Procedures. The homogeneous kinetic experiments were initiated by adding a small quantity of a stock solution of RHg*Br to a solution of Hg^0. The mixture was held at constant temperature in a thermostat and 10-ml aliquots were removed periodically. Nitrogen gas was bubbled through these vigorously for 5 min, then vapor was passed through a sulfur tower and then into a fume hood. This treatment codistilled about half of the solvent and all of the mercury. In a control experiment, this was several times the length of time necessary to remove all the Hg^0 from a saturated solution in isooctane, as judged by the ultraviolet spectrum. The volume of the demercurated aliquot was then restored to 10 ml, and the radioactivity in half of it was determined with a Nuclear-Chicago DS 5-5 well-type scintillation counter with a thallium-activated sodium iodide crystal detector. A Nuclear-Chicago Model 186 scalar equipped with an automatic timer was used to accumulate a total of at least 10,000 counts. No experiments were carried out in which the initial radioactivity was less than ten times background.

The technique for measuring heterogeneous rates was very similar to that used to measure the rate of reaction of mercury with iodine, except that the radioactivity of the samples was determined, as described above, instead of analyzing them spectrophotometrically.

Solubility Measurements. For solvents transparent in the ultraviolet, a subsaturated solution of known concentration was prepared and its spectrum determined. This was compared with the spectrum of the saturated solutions to determine their concentration. The saturated solutions were diluted as necessary. For opaque solvents the radioactivity of a solution of known concentration was determined, then the radioactivity of a saturated solution. In each solvent and at each temperature, saturation was approached from both sides; both pure solvent and supersaturated solutions were equilibrated with the crystals. Supersaturated solutions were obtained at higher temperatures. The equilibration was achieved by magnetically stirring a closed flask containing the solution and the crystals at constant temperature until no further change took place.

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(24) A. M. North, "The Collision Theory of Chemical Reactions in Liquids," Methuen and Co., Ltd., London, 1964, Chapter 3.

(25) W. B. Hales, *Phys. Rev.*, **32**, 950 (1928).

(26) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957, p 149.

(27) M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 4293 (1958).

(28) K. Torssell, *Acta Chem. Scand.*, **13**, 115 (1959).

(29) R. Criegee, P. Dimroth, and R. Schempf, *Chem. Ber.*, **90**, 1337 (1957).

(30) J. C. Sipos, H. Sawatzky, and G. F. Wright, *J. Am. Chem. Soc.*, **77**, 2759 (1955).