

deuterium content of the propanes would be between 2.0 and 2.23 deuteriums per molecule. The lower deuterium content of the propane (1.66) suggests that the reacting deuterium *on the surface* is greatly diluted by exchange with the π allyl prior to reaction. The facts that ir studies show no adsorbed hydrogen in the presence of propylene and that the isotopic analysis of chemisorbed propylene shows extensive exchange support this view. We should note, however, that although the distribution of deuterium in the propylenes approximates a random distribution for their deuterium content, the distribution of deuteriums in the propanes shows a preference for the dideuterio species. Thus, although considerable scrambling does occur in the product propanes, a preference for formation of the dideuterio species is still evident. Presumably this means that some gaseous deuterium reacts with propylene without first undergoing exchange.

If we assume the rate of addition of deuterium to propylene is first order in hydrogen, the half-time for addition is about 5 hr. This means the rate of addition of deuterium is a factor of 3 faster than exchange with propylene. This estimate, however, depends on mechanistic assumptions. We can compare the rates in still another way. For every propane molecule formed, 1.25 deuterium atoms appear in the propylene. Some of the hydrogen released on the surface by this exchange returns to the gas phase, but about one-quarter of this hydrogen (~ 0.30 /propane formed) adds to form propane; largely because of the preferential addition of this surface hydrogen, the prod-

uct propane contains only 1.66 deuteriums per propane molecule.

Conclusions. All of the reactions cited in the introduction as expected for a reactive π -allyl species were found to occur at comparable rates. Moreover, the intramolecular exchange occurs by a 1,3 shift and there is no evidence on the time scale of these experiments for exchange of the hydrogen attached to the center carbon atom. These data cannot be readily accommodated by a mechanism involving alkyl reversal but are the expected behavior for a π -allyl species. If we couple these results with the fact that addition of deuterium to propylene yields isotopic scrambling in both olefin and paraffin, as expected for a π allyl, whereas there is no such scrambling for ethylene, which cannot form an allyl species, the case is quite strong that the surface π allyl plays a major role in these reactions. This view is flawed by the occurrence of intermolecular hydrogen exchange for ethylene, for which we have no plausible interpretation, but we still feel it is valid to conclude that formation of the π allyl is an important step in all of these reactions. Such a species offers an attractive possible pathway for double-bond isomerization of higher olefins but, as yet, we have no data on this point.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We would also like to express our gratitude to the Gulf Oil Corp. for a grant that made the purchase of the deuterium-labeled propylenes possible.

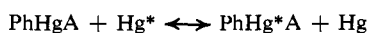
Kinetic Studies of Exchange between Metallic Mercury and Mercury Compounds in Solution. III

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Abstract: A new reaction procedure has been developed to extend the study of the isotopic exchange of organo-mercury compounds with a metallic mercury surface. This has made possible the investigation of the exchange of mercury diphenyl in a series of solvents and in the presence of surfactants. Activation parameters have been examined according to Leffler's theory and have been interpreted to indicate a difference of solvation between the transition and the ground states. A comparison has also been made between the rates of exchange of mercury diphenyl and phenylmercuric chloride with a mercury surface saturated with reactant. Both results confirm the previous postulate that the reaction proceeds *via* an *Sei* four-center reaction mechanism.

Reutov and coworkers² were the first to investigate the heterogeneous exchange of mercury and organo-mercury compounds in organic solvents



where A = Ph or halogen.

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(1) This material was presented as part of a thesis in fulfillment of the Ph.D. degree, University of London, and this author wishes to thank Sir John Cass College for a grant which made this work possible.

(2) O. A. Reutov and G. M. Ostapchuk, *Dokl. Akad. Nauk. SSSR*, **117**, 826 (1957); O. A. Reutov and U. Tan-Tsei, *ibid.*, **117**, 1003 (1957); O. A. Reutov, P. Knoll, and U. Yan-Tsei, *ibid.*, **120**, 1052 (1958); A. N.

Initially they concluded that the reaction rate was controlled by the rate of diffusion of the mercury from the metallic bulk of the surface. They therefore stirred the mercury at high speed causing it to break into droplets. Part I³ in this series of papers drew attention to the difficulty of maintaining a constant surface area of the mercury, and hence a constant rate, during stirring. This difficulty was circumvented by rigorously defining

Nesmeyanov, O. A. Reutov, and P. Knoll, *ibid.*, **118**, 99 (1958); O. A. Reutov and G. M. Ostapchuk, *Zh. Obshch. Khim.*, **29**, 1614 (1959).

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

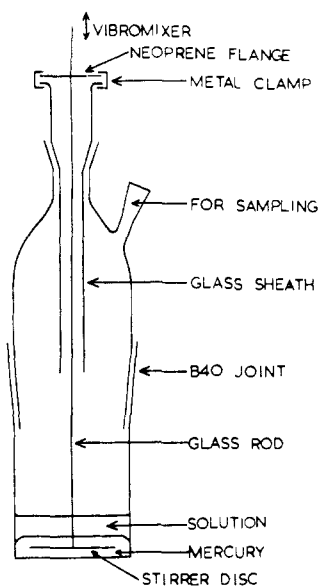


Figure 1. Vibromixer system.

the conditions of the experiment—vessel shape, stirring speed, and solvent—and limiting the selection of organomercury compounds to be examined. Reproducible results were obtained from mercury diphenyl in benzene, and from a study of a series of symmetrical substituted diaryls,⁴ it was concluded that the reaction was of the S_Ei type. Anomalous results were, however, obtained when the concentration was varied and when surfactants were added to the mixture.

When the solvent was changed or the organomercury compound structure was altered radically, there were visible variations of drop size. It was therefore decided to develop a new reaction procedure in order to extend the scope of the study and to reinvestigate the anomalies mentioned above.

Experimental Section

Materials. Mercury diphenyl (J. Sas and Co. Ltd.) was refluxed twice in benzene with decolorizing carbon and recrystallized three times from this solvent. It was dried at 60° for 15 min and then over silica gel and fused calcium chloride at a pressure of 2 mm for 24 hr. It was stored over fused calcium chloride in the dark: mp 125–126° (lit. mp 122,⁵ 125–126,⁶ 122–124°⁷).

Phenylmercuric chloride was purified, dried, and stored in a similar manner: mp 250–251° (lit. mp 252°⁸).

Benzene (May and Baker, reagent grade) was dried with fused calcium chloride and then sodium wire. It was fractionally distilled and the middle 75% distilling at 80°, was retained.

Cyclohexane (BDH, special for spectroscopy) was used for some of the experiments without further treatment. A sample was, however, purified by treatment with concentrated sulfuric acid, alkaline potassium permanganate,⁹ mercury, and sodium hydroxide.

Toluene (BDH, analar) was used for some of the experiments without further treatment. A sample was, however, purified by treatment with concentrated sulfuric acid, 5% sodium hydroxide solution,¹⁰ and mercury.

Pyridine (BDH, analar) was dried with potassium hydroxide and fractionally distilled, the middle 50%, distilling at 115°, being retained.

Nitrobenzene (BDH, analar) was dried with fused calcium chloride and fractionally distilled, the middle 50%, distilling at 209°, being retained.

Xylene (BDH) was dried with anhydrous calcium sulfate and fractionally distilled, the middle 50%, distilling at 137–138°, being retained.

Camphor (BDH, MAR) was used without further purification.

1-Dodecanol (BDH) was dissolved in ether and saturated with sodium carbonate solution. After water washing, the ether solution was dried with magnesium sulfate and the ether distilled off. The residue was fractionally distilled three times under reduced pressure.

Active Mercury. Radioactive mercury³ (1 g) containing approximately 1 mCi of ²⁰³Hg was added to 1 kg of mercury. This mercury stock was cleaned continuously by sucking filtered air through it while it was covered by dilute nitric acid. When a sample of mercury was required, it was run off from a separating funnel and passed down two columns containing deionized water (distilled water passed through an elgastat and having a resistivity greater than 4 Mohm cm). It was run straight through into the reaction vessel from a buret. Activities were estimated using a sodium iodide scintillation counter.³

Reaction Vessels. The vessels used were straight sided and flat bottomed, so that when the base was covered with mercury, the mercury/solution interfacial area was constant. This area was taken as being identical with the area of the vessel base, *i.e.*, there was no allowance for the mercury meniscus. Standard vessels of the base area 28.7 cm² were used unless otherwise indicated. They were provided with long thin necks to prevent evaporation of the organic solvent during sampling.

The vessel used for diffusion-control tests was adapted from that originally designed for the stirring experiments,³ Figure 1. The stirrer was, however, replaced by a Vibromixer (Chemap E1, Shandon Scientific Co. Ltd.), which produced vibrations in a vertical plane at a frequency of 50 cps. The amplitude was adjusted by a 2000-ohm variable resistance. The surface area of the mercury was 17.7 cm².

Reaction Procedure. The vessels containing the cleaned mercury and the organic solution were immersed in a stirred paraffin bath thermostated to $\pm 0.1^\circ$ from 20 to 100° by a bimetallic strip (Sunvic Controls Ltd.). After at least 15 min the required volume of organic solution was pipetted into the mercury vessel. Samples were then removed by pipet from the organic layer as required and counted³ in 10-ml vials. A solution of 4-ml volume was used as a standard: if the volume of the sample taken was less than this, it was made up to 4 ml with an appropriate solvent. If it was greater, then the resultant activity was corrected for change in geometry by a factor calculated from the use of solutions of known activity. The samples were clear and required no treatment for removal of colloidal mercury.

Results

Calculation of Rate. The rate of exchange, R (mol sec⁻¹), in the dynamic equilibrium of any exchange reaction can be expressed¹¹ by

$$\frac{dx}{dt} = \frac{(a+b)}{ab}(x_\infty - x) \quad (1)$$

where x is the concentration of labeled substance in one form after time t (sec), x_∞ is the concentration at infinite time, and a and b are the masses (mol) of the two substances. If $b \gg a$ and $x \ll x_\infty$, then eq 1 reduces to

$$\frac{dF}{dt} = \frac{R}{a} \quad (2)$$

where F is the exchange fraction and $100F$ is the percentage exchange.

This equation is applicable to heterogeneous as well as homogeneous reactions. The first of the two condi-

(11) A. C. Wahl and N. A. Bonner, "Radioactivity applied to Chemistry," Wiley, New York, N. Y., 1951, p 34.

(4) D. R. Pollard and J. V. Westwood, *J. Amer. Chem. Soc.*, **88**, 1404 (1966).

(5) E. Dreher and R. Otto, *Chem. Zentralbl.*, **2**, 822 (1912).

(6) M. O. Forster, *J. Chem. Soc.*, **73**, 783 (1898).

(7) R. E. Dessy and J. Y. Kim, *J. Amer. Chem. Soc.*, **82**, 686 (1960).

(8) "Handbook of Chemistry and Physics," 49th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

(9) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1959, p 163.

(10) J. H. Mathews, *J. Amer. Chem. Soc.*, **48**, 562 (1926); J. W. Williams and F. Daniels, *ibid.*, **46**, 903 (1924).

tions is satisfied in the reactions studied below since, in a typical kinetic run, the ratio mercury/organomercury compound is 300/1. The second is satisfied by plotting F against t and taking the value of dF/dt when $t = 0$.

This technique had the advantage that a series of samples could be taken from the same vessel, and also that the rate was determined before any impurities, formed in side reactions, or by decomposition of the organomercury compound, could interfere in the exchange. The value of x_{∞} was always calculated from the activity of the mercury and the concentration of mercury compound.

Purification of Mercury and Organomercury Compounds. A large number of runs were carried out using 0.1 mol l^{-1} of mercury diphenyl in benzene at 65.0° and a mercury surface area of 17.7 cm^2 without any particular purification of the mercury, although it always appeared clean. The rates of the resultant exchanges varied erratically between extremes of approximately 0.2×10^{-8} and $2.5 \times 10^{-8} \text{ mol sec}^{-1}$. When, however, the mercury was freshly cleaned with dilute nitric acid, there was a large increase in rate to $17 \times 10^{-8} \text{ mol sec}^{-1}$ for a surface area of 28.7 cm^2 under the same conditions, and the results became reproducible. The standard deviation for ten results was $1.2 \times 10^{-8} \text{ mol sec}^{-1}$.

Interfacial Agitation. The exchange rate had been increased greatly and shown to be reproducible by removal of impurities, and yet the rate-controlling step could still be diffusion of the mercury to the surface. Experiments were therefore carried out to check this possibility, using the Vibromixer (Figure 1). Kinetic runs were carried out with the mixer blade immersed in both the mercury and the organic layers. The amplitude was adjusted so that there was a continual rippling of the mercury surface, but the mercury did not break into droplets. The results (Table I) indicate that the rate is not diffusion controlled.

Table I. Effect of Agitation upon the Rate^a

Compound	Position of blade	Rate, $\text{mol sec}^{-1} \times 10^{-8}$
HgPh ₂	In Hg	13.4
	In solution	12.8
		10.8
PhHgCl	In Hg	1.48
	In solution	1.42
		1.34

^a 25 ml of 0.1 M mercury diphenyl or 50 ml of 0.01 M phenylmercuric chloride in benzene at 65.0° .

Variation of Volumes. The volumes of the solutions of the organomercury compounds were varied by a factor of 5 over a constant surface area of mercury. The resultant exchange rates were constant (Table II), indicating that there were no impurities present in small amounts which were adsorbed at the interface and which prevented the exchange. A similar result was obtained when the volume of mercury was varied by a factor of 4.

Variation of Surface Area. The rate of reaction was measured for constant volumes of mercury diphenyl and phenylmercuric chloride solutions over different surface areas of mercury varying by a factor of 8. The constancy of the ratio rate/area indicated that the rate

Table II. Effect of Volume Variation upon the Rate^a

Vol varied	Vol, ml	Rate, $\text{mol sec}^{-1} \times 10^{-8}$
HgPh ₂	10.0	17.5
	17.5	19.4
	25.0	17.5
	35.0	15.4
	50.0	15.3
PhHgCl	10.0	2.82
	15.0	2.57
	25.0	2.36
	35.0	2.47
	50.0	2.66
Hg (HgPh ₂ solution)	10.0	17.5
	25.0	18.1
	35.0	17.0
	40.0	18.3

^a 0.1 M mercury diphenyl or 0.02 M phenylmercuric chloride in benzene at 65.0° .

Table III. Effect of Variation of Interfacial Surface Area upon the Rate^a

Area, cm^2	Rate, $\text{mol sec}^{-1} \times 10^{-8}$	Rate/area $\times 10^{-10}$
	HgPh ₂	
52.8	33.3	63.1
28.7	17.5	60.9
17.7	10.8	61.2
12.6	7.84	62.4
6.2	3.20	52.0
	PhHgCl	
52.8	4.58	8.67
28.7	2.37	8.26
17.7	1.77	9.98
12.6	1.11	8.79
6.2	0.64	10.4

^a 25 ml of 0.1 M mercury diphenyl or 0.02 M phenylmercuric chloride in benzene at 65.0° .

was proportional to the surface area of the mercury for both reactions (Table III).

Variation of Concentration. The variation of the rate of exchange with concentration of mercury diphenyl and phenylmercuric chloride in benzene is shown in Table IV. The rate in each case increases with in-

Table IV. Effect of Variation of Concentration upon Rate^a

Solution	Concn, M	Rate, $\text{mol sec}^{-1} \times 10^{-8}$	k , $\text{mol sec}^{-1} \text{ cm}^{-2} \times 10^{-9}$
HgPh ₂	0.30	23.5	10.0
	0.15	22.4	11.2
	0.10	17.2	9.9
	0.05	14.1	11.3
	0.025	6.1	7.7
	0.012	5.4	12.2
PhHgCl	0.03	2.87	1.17
	0.02	2.65	1.16
	0.01	2.14	1.12
	0.005	1.52	1.07
	0.0025	1.36	1.44

^a 25 ml of mercury diphenyl or 50 ml of phenylmercuric chloride in benzene at 65.0° .

creasing mercury diphenyl concentration but approaches a maximum at high concentration. This behavior indicates that the adsorption of the organomercury

compound obeys Langmuir's isotherm.¹² The straight-line plots of concentration/rate against concentration confirmed this.

Results can thus be presented in the form of a rate constant, k , independent of the surface area S and the concentration of the species, c

$$R = kS \frac{bc}{1 + bc} \quad (3)$$

This rate constant equals the rate of exchange over 1 cm² of mercury surface saturated by reactant. The second constant, b , obtained from the above plots by the method of least squares, was found to be 15.3 l. mol⁻¹ for mercury diphenyl and 197.0 l. mol⁻¹ for phenylmercuric chloride.

Effect of Surfactants. The surfactants camphor and lauryl alcohol were added to the exchange of mercury diphenyl in benzene with stirred mercury.³ The results indicated, surprisingly, an increase in rate of exchange. This work was repeated over a still mercury surface for different concentrations of the two surfactants (Table V). The rate constant (eq 3) decreased in each case with increasing concentration of surfactant.

Table V. Effect of Surfactants on the Rate Constant^a

Surfactant	[Surfactant]	k , mol sec ⁻¹ cm ⁻² × 10 ⁻⁹
Camphor	0.039	6.52
	0.089	5.08
	0.200	5.94
Lauryl alcohol	0.037	7.99
	0.083	7.11
	0.190	5.42

^a 25 ml of 0.1 *M* mercury diphenyl in benzene at 65.0°.

Change of Solvent. The exchange of mercury diphenyl in five solvents is compared with that in benzene under identical conditions in Table VI. As the rates

Table VI. Effect of Solvent upon the Rate^a

Solvent	Rate, mol sec ⁻¹ × 10 ⁻⁸
Toluene	7.79
Cyclohexane	1.77
<i>p</i> -Xylene	4.27
Nitrobenzene	3.85
Pyridine	0.732
Benzene	17.2

^a 25 ml of 0.1 *M* mercury diphenyl at 65.0°.

were all less than in benzene, it was suspected that the reduction in rate was due to impurities in the solvent being adsorbed in the mercury surfaces and preventing exchange. Toluene and cyclohexane were therefore purified exhaustively, but the resultant rate showed no increase.

The variation of rate with concentration of mercury diphenyl was examined in toluene and nitrobenzene. In each case the rate approached a maximum with increasing concentration as in benzene. The plots of concentration/rate *vs.* concentration indicated that a rate constant, k (eq 3), could be used for the reaction.

(12) J. J. Kipling, "Adsorption from Solutions of Non-Electrolytes," Academic Press, New York, N. Y., 1965, p 39.

The method of least squares gave a value for the second constant, b , of 28.8 l. mol⁻¹ for toluene and 97.7 l. mol⁻¹ for nitrobenzene.

Activation Parameters. The rate constant for the exchange of mercury diphenyl in the six solvents and for phenylmercuric chloride in benzene were determined at five different temperatures over a temperature range of at least 20°. For those solvents in which the variation of rate with concentration had not been examined, it was assumed that the surface was saturated with mercury diphenyl at the concentration used, 0.1 *M*. The activation parameters were obtained by the usual method¹³ and are summarized in Table VII.

Table VII. Activation Parameters (per mole) at 65.0°

Solvent	ΔF^* , kcal	ΔH^* , kcal	ΔS^* , cal deg ⁻¹	$T\Delta S^*$, kcal
Mercury Diphenyl				
Benzene	32.2	17.9	-42.4	-14.3
Cyclohexane	34.0	17.8	-47.4	-16.0
Pyridine	34.6	10.5	-71.3	-24.1
Nitrobenzene	33.5	10.7	-67.3	-22.8
Toluene	32.9	9.2	-70.3	-23.9
<i>p</i> -Xylene	33.6	9.2	-72.2	-24.4
Phenylmercuric Chloride				
Benzene	33.7	14.3	-57.3	-10.4

Discussion

General. The evidence that the exchange over a still, cleaned mercury surface is not controlled by diffusion is quite conclusive. First, there are the direct agitation experiments; it is thought that the movement produced in both layers by the Vibromixer would have been great enough to have led to a very large increase in rate had the reaction been diffusion controlled. The very small increase noted was almost certainly due to the increase in surface area produced by the rippling. Second, there are the values for the enthalpies of activation; the lowest enthalpy observed was 9.2 kcal mol⁻¹ (Table VII). The value¹⁴ for a diffusion-controlled reaction normally lies between 2.8 and 6.5 kcal mol⁻¹. Finally, there are the different rates obtained for the different solvent systems at the same temperature and concentration. The rate varies by a factor of at least 20 for mercury diphenyl in the different solvents (Table VI).

It must therefore be concluded that the mercury used previously³⁻⁴ contained sufficient impurities to form a surface layer. On stirring, this surface layer was dispersed, giving the impression that the reaction was changing from the diffusion-controlled state. There is no evidence that the mercury used here was completely free from impurities. It could have contained a constant amount which was unaffected by the cleaning acid, or impurities could have been picked up before each kinetic run. However, the fact that the rate of exchange under the same conditions remained constant over at least a year's duration belies this possibility.

The rate of exchange over a clean, still surface can be compared with those we obtained previously³ using a

(13) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, p 197.

(14) L. I. Bircumshaw and A. C. Riddiford, *Quart. Rev., Chem. Soc.*, 6, 157 (1952).

stirred system. For instance, we found a rate, R , of 1.6×10^{-7} mol sec $^{-1}$ for 0.055 M mercury diphenyl in benzene using stirred mercury at 65.0°. The equivalent rate for a static mercury surface was 40×10^{-7} mol sec $^{-1}$. The rate is therefore approximately 25 times faster over the cleaned, still surface. Kreevoy and Walters¹⁵ deduced a rate constant of 0.41×10^{-5} sec $^{-1}$ for *p*-methoxyphenylmercuric chloride at low concentrations in benzene at 25°. A comparable rate constant can be deduced for the unsubstituted chloride from the data of Tables IV and VII. It is 0.018×10^{-5} sec $^{-1}$, which is slower by a factor of 22. This difference could be due to errors in the extrapolation or could be accredited to the effect of the methoxy group. It is impossible to make comparisons with the work of Reutov,² because he made no attempt to measure the surface area, and in the mercury diaryl experiments he has not reported the volumes used.

The variation of the rate of exchange with concentration (eq 3) makes comparisons between systems more complicated. For instance, it is found that the exchange of mercury diphenyl is faster than that of phenylmercuric chloride at a concentration of 0.01 M , while it is slower at a concentration of 0.001 M . To compare the reactivities of different compounds the rates must be judged when the degrees of adsorption are the same. This is done most easily by comparing the rates on surfaces saturated by reactant, *i.e.*, by the ratio of the rate constants. This ratio is 9/1 for mercury diphenyl/phenylmercuric chloride in benzene, which is contradictory to the conclusion of Reutov.²

The effect of the two surfactants upon the rate over the still mercury surface is more comprehensible. The reduction in rate can be attributed to either weak preferential adsorption on the mercury surface or to a solvent effect. It confirms our original suspicion that the very high results³ with stirred mercury were due to increases in surface area due to decreased drop size.

Solvent Effects. The initial conclusion that the variation of rate constant of mercury diphenyl with solvent was due to the solvent playing an intrinsic part in the reaction mechanism was confirmed by the wide differences in activation parameters (Table VII). It had been feared that small quantities of impurities, such as thiophene in the aromatic hydrocarbons,¹⁶ could have caused the difference in rate by preferential adsorption on the mercury surface. It should be noted that this result is in conflict with that of Reutov,² who reported that there was no solvent effect for the exchange. The result is in agreement with the work of Kreevoy and Walters,¹⁵ who found a variation in rate constant by a maximum factor of 50 for the heterogeneous exchange of substituted phenylmercuric bromide in ten solvents. However, they did not determine the relevant activation parameters.

The free energy of activation ΔF^* , and hence the rate constant, can remain nearly constant when there are large variations in the enthalpies of activation, ΔH^* , providing these are compensated by proportionate changes in the entropy of activation, ΔS^* . Benzene and cyclohexane stand out in the solvent series (Table VII) for having very high and similar values for ΔH^* . If

(15) M. M. Kreevoy and E. A. Walters, *J. Amer. Chem. Soc.*, **89**, 2986 (1967).

(16) A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience, New York, N. Y., 1955, p 318.

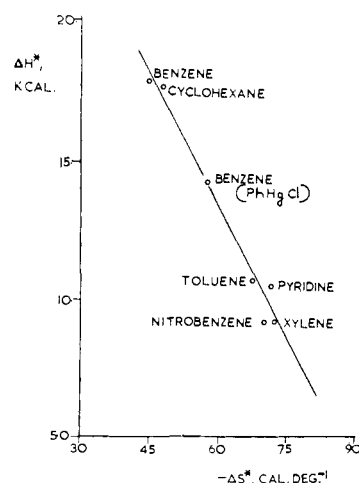


Figure 2. The isokinetic relationship.

these are taken as standards, then the changes in ΔH^* and $T\Delta S^*$ from these values for the other four solvents are such that they compensate each other. A similar compensation effect¹⁷ was observed in the homogeneous mercury diphenyl-mercuric iodide exchange.¹⁸ It was assumed that there was no solvation of the transition state when benzene and cyclohexane were used as solvents. However, in dioxane and ethanol solutions, the enthalpies of activation were nearly doubled and the entropies halved. The solution terms thus compensate one another and the reaction proceeds at approximately the same rate in all four solvents. A similar effect has been observed for the formation of hydrogen-bonded and π complexes.¹⁹ The equilibrium constants for the formation of these complexes are frequently approximately unity, giving a free energy change close to zero. For instance, the enthalpy of the iodine-*p*-xylene complex in carbon tetrachloride is -2.18 kcal and the entropy -9.60 cal deg $^{-1}$ mol $^{-1}$, and for a phenol-trimethylamine complex in cyclohexane the enthalpy is 5.7 kcal and the entropy -10.4 cal deg $^{-1}$ mol $^{-1}$.

The changes in activation parameters for the same reaction in different solvents can be examined in the light of Leffler's isokinetic relationship.²⁰ The $\Delta H^*/\Delta S^*$ data for the mercury diphenyl and phenylmercuric chloride exchanges are presented graphically in Figure 2, where it can be confirmed that a good straight line can be drawn through the various points. The method of least squares was applied and the value of the slope, β , found to be 305°K. The mean of the temperature ranges in this work was 341°K, which differs by 36°K from the value of β . This is sufficient difference for assuming that the different results were not due to experimental error. As the investigation was carried out above the isokinetic temperature, the reaction is said to be entropy controlled. The correlation coefficient for the plot was 0.98, which agrees favorably with other enthalpy-entropy relationships.²¹

The effect of experimental error upon the value of ΔH^* and ΔS^* has been examined by Peterson, Mark-

(17) K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1725 (1959).

(18) Y. K. Lee, Ph.D. Thesis, University of Cincinnati, 1960, p 107.

(19) R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **77**, 2164 (1955).

(20) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(21) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

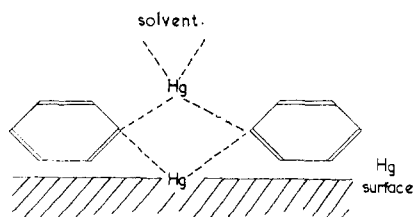


Figure 3.

graf, and Ross.²² They found that an error in ΔH^* would be directly proportionate to that in ΔS^* and that valid assumptions about the linearity of $\Delta H^*/\Delta S^*$ relationships could only be made if the ΔH^* range was greater than twice the maximum possible error in ΔH^* . For mercury diphenyl in benzene the maximum possible error in ΔH^* was 1.5 kcal, but the ΔH^* for the solvent series varies from 9.2 to 17.9 kcal, a range of 8.7 kcal mol⁻¹. A second criterion of Peterson²³ was that all the straight lines on a log k/t vs. $1/T$ plot should converge to a single point. There is no such convergence with the above data: this is not in fact surprising, as Peterson was not able to find a series which obeyed this rigid criterion, though our previous results came close to this.⁴

The mercury atom in its organic compounds forms two σ bonds and thus has two empty p orbitals available for sp² (trigonal) and sp³ (tetrahedral) complex formation. No complex of mercury diphenyl itself has been isolated yet, although there is ample evidence for their existence in solution. Oscillometric titrations have indicated the formation of 1:1 and 1:2 (mercury diphenyl:ligand) complexes with pyridine, piperidine, acetone, and ethanol among others.²⁴ The proton magnetic resonance spectrum of mercury diphenyl showed that the ortho proton interaction with ¹⁹⁹Hg was strongly dependent upon the nature of the solvent in a series which included cyclohexane, acetone, and dimethyl sulfoxide.²⁵ A shift was also observed in the uv spectrum of mercury diphenyl in ethanol and dioxane solutions, when contrasted to that in benzene and cyclohexane solutions.¹⁸ Solid complexes have, however, been isolated when the aryl group is substituted by electronegative chlorine or fluorine,²⁶ e.g., 2,2'-bipyridylbis(pentafluorophenyl)mercury.

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The six solvents used in the exchange were selected to represent a variety of coordinating powers. Pyridine and nitrobenzene were expected to coordinate strongly by donation of lone pairs from the nitrogen and oxygen, respectively. *p*-Xylene, toluene, and benzene were expected to form charge-transfer complexes, and cyclohexane was expected to be inert. The variations in enthalpy, entropy, and possibly free energy of activation with solvent will depend upon the relative degree of solvation in the transition state and the ground state. Clearly there is a difference between the two states in the solvent series, but the interpretation of the magnitude is obscure.

Mechanism. The previous papers in this series³ have discussed the mechanisms available for exchange. It was concluded that the rate-controlling step involved the formation of a four-center transition state on the mercury surface by electrophilic attack of a mercury atom. The results here are in agreement with this conclusion. Greater solvation in the transition state than in the ground state would occur if the mercury atom in the transition state were to become more electropositive, or if there was a movement away from linearity. An S_{Ei} transition state provides both a more positive mercury atom and nonlinear mercury-aryl bonds in the transition state (Figure 3).

A point arising from this work which supports electrophilic attack is the relative rate of exchange of mercury diphenyl and phenylmercuric chloride in the same solvent. If these are compared when the mercury surfaces are both saturated with reactant, then the mercury diphenyl exchange is nearly ten times faster than that of the half-salt. The electrophilic substitution of mercury diphenyl by H⁺ in methanolic hydrochloric acid solution is also much faster than that of the chloride, otherwise this latter compound would not be the product of the reaction.²⁷

Kreevoy and Walters¹⁵ have postulated an alternative mechanism for exchange of *p*-methoxyphenylmercurials with metallic mercury, involving an electron-transfer step. Their strongest argument in its favor was the relative efficiency of the surface reaction as compared to the homogeneous solution reaction involving mercury atoms dissolved in the solvent. However, it is known that the organomercury compound is attracted preferentially to the mercury surface and that any species of mercury in solution is liable to solvation, so that comparisons between the two systems are not justifiable.

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