Table III. Diamagnetic Chemical Shifts of the Ligand Protons by Extrapolation[a]

	Isoquinoline 2-oxide		Quinoline 1-oxide	
Position	$Ni(AA)_2$	$Co(AA)_2$	$Ni(AA)_2$	$Co(AA)_2$
1	524[b]	524[b]	...	...
2	...	...	511[b]	510[b]
3	489[b]	489[b]	435[b]	435[b]
4	462	462	453	454
5	468	467	465	467
6	451	453	460	459
7	457.5	457	457	458
8	458.5	460	525[b]	525[b]

[a] Shifts are in cps at 60 Mc measured downfield from tetramethylsilane as internal standard using deuteriochloroform as solvent. [b] These shifts are directly measurable on the diamagnetic ligand solutions.

spin octahedral cobalt(II) complexes.[19] The self-consistancy of the data gives support to the original assumption that the differences in the $Ni(AA)_2$ and $Co(AA)_2$ complexes isotropic shift ratios are due principally to pseudocontact terms for the $Co(AA)_2$ complex.

The observed differences between the isotropic shift ratios of the $Ni(AA)_2$ and $Co(AA)_2$ complexes of quinoline 2-oxide (Figure 2) can be qualitatively explained by assuming pseudocontact shifts for the $Co(AA)_2$ complex for a model in which rotation of the quinoline ring is hindered. Because of the steric bulk of the benzo group, protons 5, 6, 7, and 8 spend less time near the acetylacetone plane than protons in positions 2 or 3.

Figures 1 and 2 indicate that the observed ligand proton chemical shifts vary "linearly" with metal complex concentration and can be extrapolated to their diamagnetic positions at zero metal concentration. This procedure was used in obtaining the isotropic shifts. Quantitatively this relationship is described by eq 3, where the $\Delta\nu$'s are redefined as chemical shifts rather than isotropic shifts, which is the expression defining chemical shifts of a system in rapid equilibrium.[20] Linearity can be expected in such a labile system in which each increment of added paramagnetic ion is completely converted to a single type of paramagnetic complex, to a constant ratio of different complexes, or to a variable ratio of complexes having identical stoichiometry and chemical shift. The validity of such a linear dependence is shown in the present work, within the limits of experimental uncertainties, using the chemical shifts readily available from the spectra of the diamagnetic ligands. The diamagnetic chemical shifts obtained by extrapolation are given in Table III. Although this method for obtaining chemical shifts should be applicable to any rapid equilibrium, it is particularly useful for molecules which coordinate with paramagnetic ions because of the very large shifts which are found in these systems. In the present work the shifts observed are due to spin delocalization by a π mechanism, and for the $Co(AA)_2$ complexes these shifts are also due to pseudocontact interactions. Earlier Phillips, Looney, and Ikeda[21] also noted a linear dependence of the methyl and methylene proton resonances in 1-propanol with paramagnetic metal ion concentration, a system which involves spin delocalization by a σ mechanism.

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(20) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1954).

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

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Contribution from the Department of Chemistry, Sir John Cass College, London, England. *Received August 20, 1965*

Abstract: Further investigations of the conditions affecting the exchange of diarylmercury in solution with metallic mercury have been performed using a variety of symmetrically monosubstituted mercury diaryls. Activation parameters ΔS^*, ΔH^*, ΔF^*, E_A, and log PZ have been determined for ten compounds, and the theories of Hammett and Leffler applied to show that all reactions follow a constant S_Ei mechanism throughout the series. Measurements of reaction surface area have been made and are considered in the light of log PZ values obtained.

In part I of this study, a report was made of an experimental technique for the exchange of diphenylmercury in benzene solution with a stirred metallic mercury layer.[2] This followed an initial report by Reutov and Ostapchuk.[3] Experimental parameters involved were investigated in turn by us, and the reaction was shown to proceed reproducibly and reversibly with first-order kinetics under conditions involving sufficient stirring. The reaction rate was shown to depend directly upon the mercury surface area, though no

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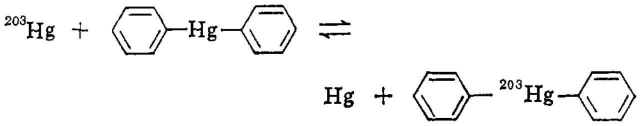
(1) Part of this material was taken from a thesis of D. R. Pollard in fulfillment of the degree of Ph.D., University of London, at Sir John Cass College.

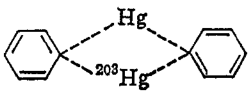
(2) D. R. Pollard and J. V. Westwood, *J. Am. Chem. Soc.*, **87**, 2809 (1965).

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

method was available for its absolute measurement. It was concluded that the process was a simple exchange proceeding according to the equation



Using an unsymmetrical mercury aryl compound for exchange, the only products isolated were chemically identical with the starting materials, and therefore a bridge transition state was proposed of the type



Investigation of the variation of reaction rate with mercury aryl concentration revealed anomalous results, and an explanation was made in terms of product inhibition of reaction. Using substituted mercury aryl compounds, the reaction rate should vary with the structure of the compound used. Change of hybridization due to solvent coordination should modify the reaction rate and vary with the type and position of substituents placed on the mercury aryl ring systems. The mechanism of the adsorption process may also be affected by changing ring substituents.

Reutov and Nesmeyanov[4] and Ingold[5] have made detailed studies of the mechanism of homogeneous mercury aryl exchange reactions. These have been found to follow paths involving electrophilic substitution. Ingold in particular has classified the possible reaction types into three classes SE1, SE2, and SEi.[5] In view of the similarity of the process to those previously investigated, it seemed reasonable to suppose that an electrophilic mechanism was also involved in this study, and it was vital to check this and to determine which reaction type was in operation.

The present study investigates these factors by measurements of activation parameters using variously substituted mercury diaryl compounds and their interpretation in the light of the theories of Leffler[6] and Hammett.[7] Attention was restricted to mono symmetrically substituted mercury diaryls in order to simplify the theoretical treatment. As the surface area must appear in the rate equation, it was important to devise a method for its determination so that the experimental activation parameters might be compared with those theoretically predicted. Photographic counting techniques have been employed in this context.

Experimental Section

1. Materials. Dibenzylmercury was prepared from benzyl bromide by conversion to the Grignard reagent, reacting with mercuric chloride in ether–benzene solution, and decomposing with aqueous hydrochloric acid. The product was extracted with and recrystallized from benzene: mp 109°, lit 104°,[8] 110–111°.[9]

Di-*o*-chlorophenylmercury was prepared from *o*-bromochlorobenzene by a Grignard reaction in a manner similar to that of dibenzylmercury: mp 146°, lit[10] 146–147°.

Di-*m*-chlorophenylmercury was similarly prepared from *m*-bromochlorobenzene: mp 147.5–148°, lit[11] 148–149°.

Di-*p*-chlorophenylmercury was similarly prepared from *p*-bromochlorobenzene: mp 249–251°, lit 242–243°,[12] 249–252°.[13]

Di-*o*-tolylmercury was prepared from *o*-bromotoluene by a similar procedure, but an additional stage involving refluxing with potassium iodide solution was necessary as the above procedure produced a large proportion of the corresponding arylmercury chloride.[14] The product was recrystallized from alcohol: mp 100–101°, lit[15] 106.5–107°.

Di-*m*-tolylmercury was prepared from *m*-bromotoluene by the above Grignard method. Purification and recrystallization were from chloroform solution: mp 103–104°, lit[14] 102°.

Di-*p*-tolylmercury was prepared from *p*-bromotoluene similarly and purified by three recrystallizations from benzene: mp 243°, lit 238°,[7] 243–244°.[16]

Di-*o*-methoxyphenylmercury was prepared from *o*-bromoanisole by a similar method, but this also involved additional aqueous potassium iodide treatment. The product was recrystallized from alcohol: mp 106–108°, lit[17] 108°.

Di-*p*-methoxyphenylmercury was prepared by reduction of *p*-bromoanisole by an 8% sodium amalgam in the presence of ethyl acetate as catalyst. The product was recrystallized three times from benzene: mp 200–202°, lit 200°,[18] 200–202°.[19]

Radioactive mercury was produced by irradiation of A.R. mercury in silica ampoules in the pile BEPO (Harwell, England), using thermal neutrons at pile factor 4 for 2 days. The irradiated mercury, 1 g, after allowing for decay of short-lived impurities and containing 500 μcuries of ^{203}Hg, was added to 100 g of inactive mercury; 1 g of this solution was added to 500 g of inactive mercury to form what is termed the stock solution.[2]

Benzene, used as reaction medium, was purified as follows. Pure and crystallizable benzene (Harrington) was dried with sodium wire and fractionally distilled from the all-glass apparatus, collecting the fraction of bp 79–81°.[20]

2. Reaction Procedure. Exchange reactions between active mercury and diaryl compounds in solution were carried out in vessels described in part I of this series.[2] These were thermostated in an oil bath which could be maintained to ±0.1° up to 95° by a mercury–toluene regulator system. For each kinetic run 75.00 ± 0.01 g of the mercury stock solution was used with 20-ml portions of the diarylmercury solution in benzene. Kinetic runs were carried out in duplicate.

3. Radiation Counter. A single 11-stage photomultiplier tube (E.M.I. 6097B) was used with a Hilger and Watts 2 in. × 1.75 in. well sodium iodide crystal as detector, and is described in detail in part I. The same E.H.T. unit, scaler, timer, and amplifier (Panax Equipment Ltd.) were used, and the counter operating conditions carefully selected in part I were adopted throughout this work. These were amplifier gain × 50, E.H.T. 1200 v, and discriminator voltage 18 v. Counter performance was checked daily using a reference source of 3 ml of ^{137}Cs solution sealed into a glass vial (4.7×10^2 disintegrations/sec/ml, A.E.R.E., Harwell, England), which gave a counting efficiency of 48% for ^{137}Cs.

4. Sampling and Counting Technique. After reaction the benzene layer was removed from each reaction vessel and passed through a 3-cm column of alumina to remove suspended mercury. The benzene was evaporated off in a stream of dry air and a portion (*ca.* 0.3 g) of the residue was accurately weighed into a clinical type counting vial; 4 ml of pyridine was then added and the vial counted by insertion into the detector crystal well.

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(4) O. A. Reutov and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 655 (1953).

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Results

Reaction Kinetic Parameters. All the mercury aryl compounds studied gave a linear plot of $-\ln(1 - F)$ *vs.* t, where F is the fraction of the total exchange occurring in time t, *i.e.*, S_t/S_∞, where S is specific activity. Consequently all obeyed the relationship $kt = -\ln(1 - F)$, where k is a rate constant in units of sec^{-1}. S_∞ was obtained from the exponential plot of S_t *vs.* t, using the method of Guggenheim[21] and Smith.[22] Typical results are shown in Table I for di-*p*-chlorophenylmercury.

Table I. Exchange Kinetics for Di-*p*-chlorophenylmercury

Temp, ±0.1°K	Reaction time, hr	Sp act, counts/sec/g	−Log (1 − F)
303.2	1.0	12.7	0.0735
	2.0	21.9	0.2439
	3.0	37.3	0.2768
	4.5	46.0	0.3870
	∞	78.5	...
313.2	0.5	12.3	0.0566
	1.0	33.1	0.1908
	2.0	48.4	0.3194
	3.0	61.9	0.4837
	4.5	72.9	0.6989
	∞	91.8	...
323.2	0.5	24.5	0.1307
	2.0	68.4	0.5593
	3.0	75.0	0.7334
	4.5	86.6	1.1844
	∞	92.6	...
333.2	0.5	28.8	0.1358
	1.0	53.0	0.2899
	2.0	80.3	0.5839
	3.0	94.2	0.8573
	4.5	104.6	1.3847
	∞	108.4	...
343.2	0.5	41.3	0.2073
	1.0	74.3	0.5019
	2.0	102.8	1.2781
	3.0	107.1	1.3952
	∞	108.5	...

Summarized values of rate constants and log PZ values for the mercury diaryl compounds considered are shown in Table II.

The activation energy values E_A were obtained from the plot of log k *vs.* $1/T$, and the free energy ΔF^*, enthalpy ΔH^*, and entropy of activation ΔS^* were calculated in each case using the usual thermodynamic equations.[23] A summary of the kinetic and thermodynamic data at 60° is given in Table III.

Determination of Surface Area. For a surface reaction the Arrhenius equation becomes

$$k = P\bar{n}se^{-E_A/RT} \qquad (1)$$

where P is the probability factor, $\bar{n}$ is the number of particles per second striking 1 cm^2 of the surface, and s is the actual surface area involved in reaction. $\bar{n}$ is given by the expression

$$\bar{n} = \frac{W\bar{c}}{\phi\sqrt{6\pi}}$$

Table II. Summary of Experimental Exchange Kinetic Data

Compound	Temp, ± 0.1°K	5 + log k	Log PZ	% reaction followed
Diphenylmercury	303.2	0.1461	5.505	16
	313.2	0.4314	5.451	27
	323.2	0.5843	5.294	48
	328.2	0.7597	5.319	58
	333.2	1.1523	5.571	92
	343.2	1.3222	5.467	97
Di-*o*-chlorophenylmercury	328.2	0.7076	7.008	66
	333.2	0.8865	7.016	71
	338.2	1.1206	7.091	88
	343.2	1.2380	7.048	94
	348.2	1.3160	6.968	97
Di-*m*-chlorophenylmercury	328.2	0.5599	6.995	38
	333.2	0.7076	6.972	56
	338.2	0.9638	7.061	77
	343.2	1.1139	7.054	89
	348.2	1.2041	6.984	92
Di-*p*-chlorophenylmercury	303.2	0.7614	3.290	59
	313.2	1.0043	3.292	80
	323.2	1.2253	3.288	93
	333.2	1.2765	3.107	96
	343.2	1.6057	3.257	97
Di-*o*-tolylmercury	324.2	1.0682	3.177	77
	328.2	1.1987	3.221	82
	338.2	1.3579	3.173	90
	348.2	1.5775	3.195	98
Di-*m*-tolylmercury	323.2	0.9294	3.535	67
	328.2	1.1072	3.591	90
	333.2	1.2405	3.617	94
	343.2	1.4166	3.579	98
	350.0	1.5250	3.548	97
Di-*p*-tolylmercury	333.2	1.3181	5.728	86
	338.2	1.4553	5.728	87
	343.2	1.6212	5.760	95
	348.2	1.6599	5.673	96
Di-*o*-anisylmercury	333.2	1.2878	5.978	83
	338.2	1.4166	5.957	94
	343.2	1.5988	5.999	97
	348.2	1.7042	5.969	97
Di-*p*-anisylmercury	333.2	1.4511	4.701	96
	338.2	1.5351	4.661	98
	343.2	1.6891	4.708	97
	348.2	1.7459	4.636	98
Dibenzylmercury	323.2	0.1139	9.304	3
	328.2	0.4624	9.432	6
	339.2	0.6021	9.141	8
	343.2	1.0170	9.377	11
	349.2	1.1673	9.337	13

Table III. Summary of Kinetic and Thermodynamic Data at 60°

Compound	E_A[a]	5 + log k[b]	ΔH^*[a]	ΔF^*[a]	$-\Delta S^*$[c]
Diphenylmercury	14.3[d]	1.1523	13.6[d]	25.3[d]	35.1[d]
Di-*o*-chlorophenylmercury	16.9	0.8865	16.2	25.7	28.5
Di-*m*-chlorophenylmercury	17.1	0.7076	16.4	26.2	29.4
Di-*p*-chlorophenylmercury	10.4	1.2765	9.7	25.4	46.9
Di-*o*-tolylmercury	10.5	1.280[e]	9.8	25.1	45.9
Di-*m*-tolylmercury	11.2	1.2405	10.5	25.2	44.0
Di-*p*-tolylmercury	14.3	1.3181	13.6	26.1	37.5
Di-*o*-anisylmercury	14.7	1.2878	14.0	25.1	33.4
Di-*p*-anisylmercury	12.5	1.4511	11.8	24.9	39.2
Dibenzylmercury	20.9	0.048[e]	20.2	27.0	20.3

[a] In kcal. [b] $-k$ in 10^4 sec^{-1}. [c] In cal mole^{-1} deg^{-1}. [d] See ref 2. [e] Interpolated value from plot of log k *vs.* $1/T$.

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(21) E. A. Guggenheim, *Phil. Mag.*, 2, 538 (1929).

(22) R. C. Smith, *ibid.*, 1, 382 (1926).

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

where W is the number of particles in a total of N species (solute and solvent), $\bar{c}$ is the root-mean-square velocity of a particle, and ϕ is the molecular covolume of the solution.

To use eq 1 for calculating kinetic parameters and thereby check theoretically the results obtained in part I and in this paper, some knowledge of the surface area of the reaction interface was required. It was noted that during reaction all the mercury was transformed into very small droplets within about 30 sec of the commencement of stirring. Distribution of drop size was small when the layer was maintained in constant agitation. Following reaction on stopping the stirrer, these droplets settled rapidly but did not coalesce for several hours if not removed from the surrounding liquid. If, however, the film of solution adhering to the drops was allowed to evaporate, then the drops rapidly coalesced into larger ones. Evaluation of the reaction surface area was performed as follows. A sample of the settled mercury layer was removed by plunger pipet, placed on a watch glass, and rapidly photographed on fine grain, 35-mm film, using a single lens reflex camera and extension tubes. The photographs were enlarged to give prints of magnification approximately ×10. A typical example of one of these is shown in Figure 1. The number of drops in each specimen was counted visually. The samples were then washed with benzene to remove adhering mercury diaryl, dried, and weighed. Specimen results obtained for a number of diaryl mercury compounds at typical temperatures and concentration are shown in Table IV.

Table IV. Evaluation of Reacting Mercury Surface Area

Compound[a]	Temp, °C	No. of drops counted	Av drop weight, g × 10^4
Diphenylmercury	40	1275	2.49
	40	443	2.33
	60	1261	2.01
	60	323	1.98
Dibenzylmercury	40	352	1.89
	40	467	2.14
	60	513	2.73
	60	84	2.13
Di-*m*-tolylmercury	40	842	2.56
	40	904	2.31
	60	1121	1.94
	60	676	2.18
Di-*p*-anisylmercury	40	754	2.53
	40	351	2.21
	60	633	2.07
	60	521	2.10

[a] The concentration of the mercury aryl solution was 0.05 *M*.

In spite of the apparent crudity of the method, the results show reasonable consistency. Out of a total of 23 measurements, the maximum and minimum values recorded were 2.73×10^{-4} and 1.89×10^{-4} g, respectively. These differences are probably not significant in view of the errors involved in the method. From the results of Table IV it is reasonable to take an average drop weight of 2.24×10^{-4} g, and on the basis of this the surface area of 75 g of mercury at 60° may be calculated to be 899 cm^2.

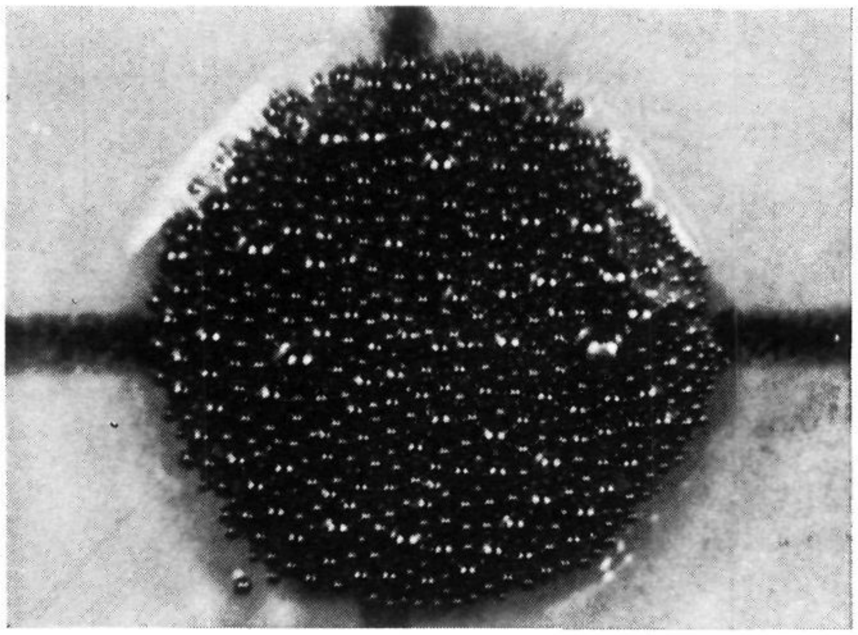

Figure 1. Photograph of a sample of the mercury droplets.

Discussion

Interpretation of Log *PZ* Values. There are two approaches to the consideration of frequency factors, represented by the collision and absolute rate theories of reaction rates. It is instructive to compare the theoretical results with those obtained experimentally. The collision theory relates the frequency factor to the number of solute molecules striking the surface per second. If the concentration of reactants is sufficient for complete coverage of the surface with adsorbed molecules and assuming that every solute molecule striking the surface reacts, the *PZ* term of the Arrhenius equation should be identical with the number of collisions per second with the surface. It may be shown[24] that for dilute solution the number of moles striking the interface per second

$$X = cA\sqrt{\frac{RT}{2\pi M}}$$

where c = the concentration of mercury aryl solution in mole/cc, and A = the area of the interface in cm^2.

Taking as a typical example diphenylmercury at 0.05 mole/l. and 60° reacting over a mercury surface area of 899 cm^2, $X = 3.1 \times 10^3$ moles/sec.

From the theory of absolute reaction rates we may deduce[23] that for an adsorption process

$$v = c_{\mathrm{a}}\frac{k^*T}{h}\frac{f^*}{f^a}e^{-(\epsilon_0 + \epsilon)/k^*T}$$

$(\epsilon_0 + \epsilon)$ is the true activation energy, whereas ϵ_0 is the apparent activation energy, and the measured E_{A}, and constitutes the difference in energy between the unadsorbed reactants and the activated state. Assuming that the partition functions f^* and f^a are unity and ϵ is small, we may approximate to

$$v = c_{\mathrm{a}}\frac{k^*T}{h}e^{-E_{\mathrm{A}}/RT}$$

Thus the *PZ* term of the Arrhenius equation here equals $c_{\mathrm{a}}(k^*T/h)$, where c_{a} is the concentration of adsorbed molecules. This is difficult to measure directly but, when the surface is completely covered, may be approximated to the number of adsorption sites of the

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(24) R. P. Bell, *J. Phys. Chem.*, **32**, 882 (1928).

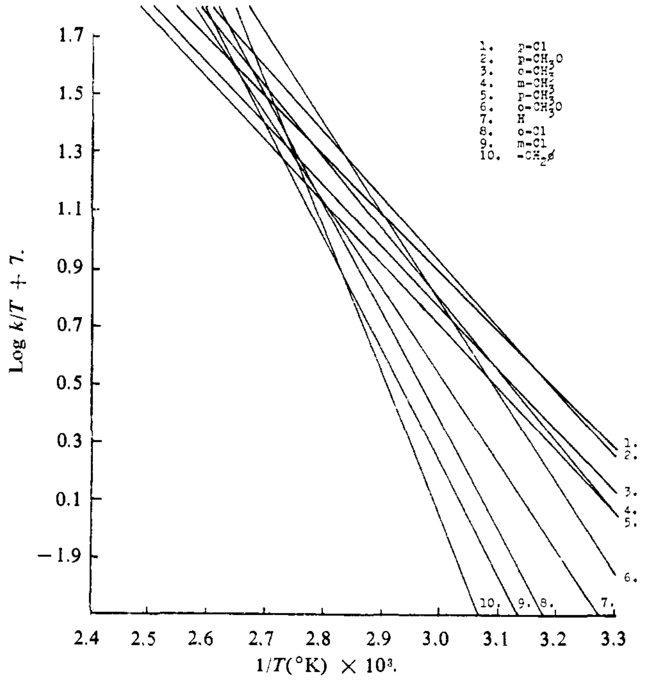

Figure 2. Petersen presentation of isokinetic data.

surface per cm². From experience this is of the order of 10^{15}. Therefore, taking the same typical conditions as before $c_a(k^*T/h) = 1.3 \times 10^{10}$ moles/sec.

There is a difference in approach between these two methods. The collision theory considers as reactants the solute striking the surface, while the absolute rate theory takes the mercury aryl molecules after adsorption as reactants. However, the experimental values lie between the two extremes. The lower ones are of the order of those predicted by the collision theory, and thus $P \geqslant 1$. This is surprising, as it is not possible that the molecules should all strike the surface in the correct orientation to allow exchange, and thus P should be less than unity.

Consideration of the adsorption process by the absolute rate theory results in the surface appearing "sticky," *i.e.*, molecules which strike the surface may be held there pending reaction; the longer the molecule is held on the surface, the more likely it will be to rearrange to an orientation allowing exchange.

Generally the adsorption process is not well understood. However, it seems significant that in Table II, log *PZ* values for *ortho* and *meta* isomers resemble each other, while those for *para* compounds differ and are generally lower than other isomers. It is probable that the "sp" linear hybrid normally associated with the mercury aryl molecules is modified in solution to an approximately "sp³" type by solvation.[18,25] Results suggest that steric hindrance of reaction by *ortho* groupings is not as important as hindrance of the adsorption process by *para* substituents in any consideration of the change of rate due to changing substituent.

Effect of Substituent Groups. It has become customary to interpret the effect of substituent groups in terms of the isokinetic relationship put forward by Leffler,[26] *i.e.*, as

$$\Delta F^* = \Delta H^* - T\Delta S^*$$

if

$$\Delta H^* = \Delta H_0^* + \beta\Delta S^*$$

then

$$\Delta F^* = \Delta H_0^* - (T - \beta)\Delta S^*$$

which constitutes an isokinetic relationship, where β is an isokinetic temperature. This has lead to an interpretation of the relationship in terms of a plot of ΔH^* *vs.* ΔS^*. Petersen, Markgraf, and Ross[27] and Petersen[28] have questioned the validity of interpreting such linear relationships, established by means of a correlation coefficient, as proof that an isokinetic relationship exists. They point out that both ΔH^* and ΔS^* are derived quantities and the values are obtained from a single equation, and suggest random error could well give rise to just such linearity. They propose that it is better to establish the existence of the relationship by a series of intersecting log (k/T) *vs.* $1/T$ plots. This can be justified from the absolute reaction rate theory assuming a simple reaction path and a transmission coefficient of unity.

Such a plot has been made from the data of Table II and is shown in Figure 2. It is clear that within the limits of the experimental error² the lines tend to a common intersection in the region of 365°K. This may be taken as sufficient proof that an isokinetic relationship holds for this reaction. As yet it does not seem possible to evaluate further results expressed in this form, owing mainly to mathematical inadequacies and the absence of similarly presented results by other authors for the purposes of comparison. Having shown the reality of the relationship, it is therefore reasonable to return to a plot of ΔH^* *vs.* ΔS^*. This is shown in Figure 3 and conforms to a straight line, with correlation coefficient 0.979. From the slope of this plot the isokinetic temperature is 384°K. The results thus show that the experimental temperature is far enough away from β for substituent effects to have a real significance in values of ΔH^* and ΔS^*, while not being so far removed as to invalidate the relationship by changes in ΔH^* with T. It may be concluded that a constant mechanism applies throughout the series. As reaction takes place below the isokinetic temperature, it is enthalpy controlled rather than entropy controlled. The large changes in the values of ΔS^* are at first surprising. However, they are in line with results obtained in other processes involving mercury diaryls, where changes in hybridization from sp to sp³ due to solvation may be proposed.[18] Thus the largest degree of ground-state solvation would be expected for aryl compounds containing electron-withdrawing substituents. This solvation should be retained in the transition state yielding a high entropy term. For aryl molecules having attached electron-donating groups, solvation should be less in the ground state and should become more appreciable in the transition state, leading to a low entropy term. This is generally borne out by the values recorded in Table III. Similarities of *ortho* and *meta* isomers as compared with the *para* ones are again noted. It is also significant

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(25) W. G. Schneider and A. D. Buckingham, *Discussions Faraday Soc.*, 34, 147 (1962).

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

(27) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, 83, 3819 (1961).

(28) R. C. Petersen, *J. Org. Chem.*, 29, 3133 (1964).

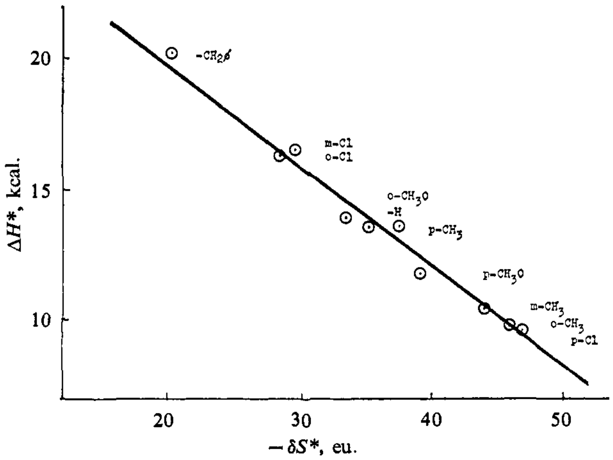

Figure 3. The isokinetic relationship.

that the dibenzyl compound fits the plot, and thus its reaction follows the same mechanism. It would be expected that while this molecule would take up a similar transition state, resonance interaction with the ring systems would be effectively blocked.

It is appropriate to try to apply the Hammett relationship[7] to these reactions. Though the condition for the Hammett relationship ($\Delta\Delta S^* = 0$) to hold is not applicable, we have shown that ΔH^* varies linearly with ΔS^*. This constitutes a sufficient condition for the application of the relationship.[6,26,29] Hammett substituent constants σ and the modified electrophilic substituent constants σ^+ [30] were plotted *vs.* log k for the *ortho* and *para* isomers employed (Figure 4). Apart from the *p*-chloro compound, a good linear plot was obtained from the σ-type constants with correlation coefficient 0.998. Attack may differ in nature at each ring system,[30] and a substituent constant $(\sigma + \sigma^+)/2$ may express more accurately the reaction.[18] A plot using this constant however gave a correlation coefficient of only 0.895; thus the best plot is represented by the use of the σ values. From the slope of this plot, the reaction constant ρ at 60° is -1.0. The reaction is therefore electrophilic in character. Other values of ρ, *i.e.*, -2.8[18] and -1.0,[31] have been reported for reactions of diarylmercury compounds in solution; values of this type indicate a reaction of fairly weak electrophilic nature.

Petersen, *et al.*,[27,28] note that they had been unable to find a clearly valid linear ΔH^*, ΔS^* relationship in the literature. There is evidence to show that this may be due to a lack of a realization that a separate consideration of internal, *i.e.*, electrometric influences, and external, *i.e.*, solvent-influenced effects, should be undertaken. Hepler[32] and other authors[33] go so far as to write

$$\Delta H^* \equiv \Delta H_{\text{int}} + \Delta H_{\text{ext}}$$

$$\Delta S^* \equiv \Delta S_{\text{int}} + \Delta S_{\text{ext}}$$

The Hammett relationship considers by definition the effect of substituents on reaction rate and is thus concerned with the change of ΔH_{int} and ΔS_{int}. The Leffler ΔH^*, ΔS^* plot may be applied to either internal or external contributions, but it is clear that simultaneous changes in both may be reflected in a nonlinear plot. As the sequence of points on the isokinetic line is irregular and uncorrelated with the free energies, there should be two interaction mechanism vectors.[34] The experimental deviations could be accounted for if one of these was an experimental error vector, and the effect of solvent modification of hybridization constant throughout the series of compounds taken, *i.e.*, $\Delta H_{\text{ext}} = 0$, $\Delta S_{\text{ext}} = 0$. Alternatively, there may be two real interaction mechanisms, one a true substituent effect on the adsorption process, and the other, for instance, due to the effect of solvent on the reaction after adsorption. A similar investigation of the exchange of a single compound in a variety of solvents could yield information on these external terms, and this is now being carried out.

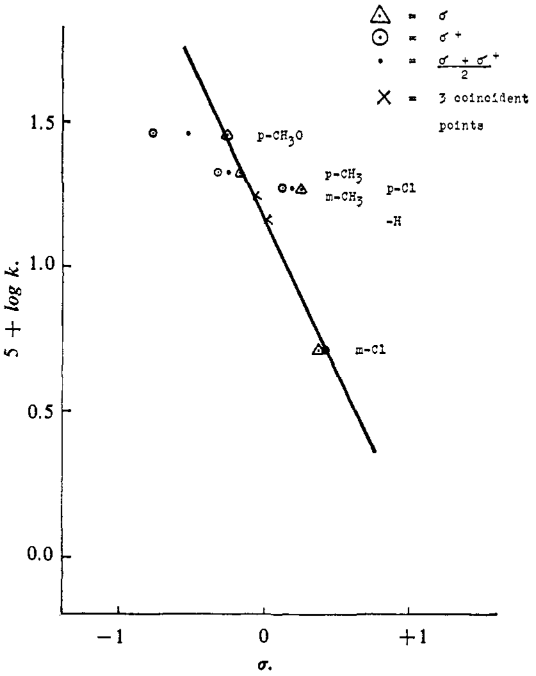

Figure 4. Hammett plot.

This evidence is all consistent with attack by an electrophilic species at the carbon atom bonded to the mercury atom. For an electrophilic reaction, electron-releasing ring substituents will increase the rate, and electron-attracting groups will cause a decrease. An examination of Table II shows that this is indeed the case and that substituents are, in order of decreasing rate, $CH_3O > CH_3 > H > Cl >$ benzyl. We should also expect *ortho* > *para* > *meta* in any series of isomers. However, we observe *para* > *ortho* > *meta*. This anomaly could be accounted for either by the steric effect of the *ortho* grouping on the reaction path or the interaction of the *para* grouping with the surface during

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(30) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

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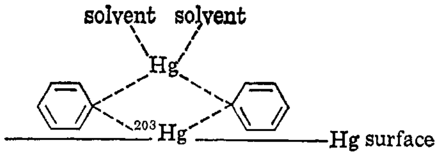
(33) L. G. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963); M. Born, *Z. Physik*, **1**, 45 (1920); R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

(34) J. E. Leffler and E. Grunwald, "Notes and Equilibria of Organic Reactions," John Wiley and Sons Inc., New York, N. Y., 1963, p 342.

the adsorption process. Further experimental work with bulky groups in these positions is in progress. Though the reaction must be bimolecular with one reactant in excess, it is difficult to envisage any simple SE2 mechanism as this would involve the detachment of one of the rings, contrary to the results obtained with *p*-nitrophenylphenylmercury in part I. The only way to completely substitute the mercury atom is by two successive SE2 type processes during which any one ring is never completely detached, *i.e.*, a type of SEi mechanism. As the products are essentially similar to the reactants, the potential energy diagrams should be symmetrical about the transition state. This must be postulated as



which is similar to that proposed by Reutov.[3] The use of the substituent constant $(\sigma + \sigma^+)/2$ implies successive attack at each ring. However, the best Hammett plot was obtained using σ constants, so that it seems more likely that attack on both rings is virtually simultaneous, the van der Waals adsorption forces leading to chemical bonds in the transition state.

The Vibrational Spectrum of the Hydrolytic Hexamer of Bismuth(III)[1a]

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Abstract: The Raman spectrum of hydrolyzed bismuth(III) perchlorate solutions and both Raman and infrared spectra of crystalline samples obtained from these solutions are reported. The clear agreement of solid and solution Raman spectra establish the similarity of the structural units in both phases. The spectral features are satisfactorily interpreted as arising from the normal vibrational modes of the octahedral cage complex, $Bi_6(OH)_{12}^{6+}$. There is no vibrational evidence for perchlorate binding either in solution or in the solid.

In recent years there has been a great deal of interest in the hydrolytic polymerization of metal ions. Along with the exhaustive potentiometric studies of Sillén and his co-workers,[2] which have established the near universality of polynuclear complex formation accompanying metal ion hydrolysis, there have been several investigations aimed at characterizing the polynuclear products by other methods. Ultracentrifugation,[3] light scattering,[4] and the coagulation method[5] have been applied to this task. Vibrational spectroscopy offers attractive possibilities in this direction, especially for the structural elucidation of hydrolytic polymers. To date these possibilities have been little explored, but a beginning has been made in the application of Raman spectroscopy.[6,7]

The hydrolysis of bismuth(III) has been particularly well characterized. Olin's potentiometric study,[8] the ultracentrifuge measurements of Holmberg, Kraus, and Johnson,[3] and the light scattering results of Tobias and Tyree[4] are all in agreement that a single hydrolysis product, $Bi_6(OH)_{12}^{+6}$, predominates over a wide range of bismuth and hydrogen ion concentrations in perchlorate solution. Danforth, Levy, and Agron,[9] using solution X-ray scattering, established the structure of this complex as an octahedral array of bismuth ions bridged by hydroxyl groups, which are most probably located at each edge of the octahedron, although the bismuth–oxygen interactions could not be determined with precision. The high concentrations of hydrolyzed bismuth attainable in perchlorate solution and the high atomic weight of bismuth should ensure favorable intensities for Raman scattering, assuming some covalency for the bismuth–oxygen bonds. Consequently, we decided to begin a program of vibrational spectroscopic studies of metal ion hydrolysis with this system.

Experimental Section

Two solutions of bismuth(III) were prepared by dissolving reagent grade Bi_2O_3 (Baker and Adamson) in concentrated perchloric acid with overnight digestion to complete dissolution. Solution I was 4.87 *M* in bismuth and 6.85 *M* in perchlorate; solution II was 8.41 *M* in bismuth and 8.85 *M* in perchlorate. Solid samples for both Raman and infrared measurements were obtained by slow crystallization from solutions I and II. The crystals were ground to a fine powder in an agate mortar. The powder was pressed to remove excess perchloric acid, dried in an oven at

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[1] (a) This investigation was supported in part by the National Science Foundation under Grant GP-3404 and in part by the Public Health Service under Grant GM-13498-01 from the National Institute of General Medical Sciences; (b) NASA Predoctoral Fellow.

[2] See L. G. Sillén, *Quart. Rev.* (London), **13**, 146 (1959), for an early review. An example of recent work is G. Biedermann and L. Newman, *Arkiv Kemi*, **22**, 203 (1964).

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