THE REACTION OF DIPHENYLMERCURY AND CARBON TETRACHLORIDE AT A MERCURY SURFACE

R. A. G. MARSHALL* AND D. R. POLLARD

Department of Chemistry, Sir John Cass College, London (Great Britain)

(Received July 6th, 1970)

SUMMARY

A new reaction between diphenylmercury and carbon tetrachloride on a mercury surface leading to phenylmercuric chloride has been identified. The process has been investigated using labelled metallic mercury and the results confirm the existence of an S_Ei transition state similar to that previously postulated for heterogeneous exchange reactions of mercury.

INTRODUCTION

Considerable work has been carried out on the heterogeneous exchange reactions of organomercury compounds and metallic mercury[1,2],

$$PhHgA + Hg^*(m) \rightarrow PhHg^*A + Hg(m)$$
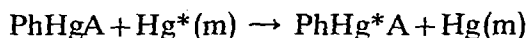
where A = Ph or halogen.

The most recent development has been the exploitation of a new experimental technique to study solvent effects with the diphenylmercury exchange[3]. It was concluded that the degree of solvation of the mercury atom was different in the transition state from the ground state. It is now shown that in carbon tetrachloride, the solvation of the diphenylmercury transition state is so strong that phenylmercuric chloride is formed.

The reaction of diphenylmercury with carbon tetrachloride alone has been reported under conditions when free radicals could be generated e.g. in UV light[4],

$$Ph_2Hg + 2\ CCl_4 \rightarrow PhHgCl + C_2Cl_6 + PhCl$$
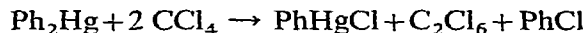
or in the presence of peroxides[5]

$$Ph_2Hg + CCl_4 \rightarrow PhHgCl + PhCCl_3$$
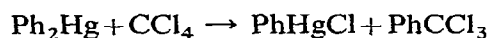
However no report of the present reaction exists in the literature.

---

* Present address: Department of Chemistry, Woolwich Polytechnic, London, S.E. 18.

EXPERIMENTAL

Materials

Diphenylmercury was refluxed twice in benzene with decolourising carbon and recrystallised three times from the same 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 h.

1 kg mercury was cleaned continuously with dilute nitric acid, agitation being by means of a stream of air. When a sample was required it was run off into a separating funnel and washed using two columns of deionised water to remove the acid. It was labelled by the addition of 1 mCi [203]Hg as 1 g of mercury metal.

Carbon tetrachloride (B.D.H., Analar) was used for most of the experiments without further treatment. A sample was however purified[6] by refluxing with three portions of 5% sodium hydroxide solution, washing with water and then stirring with 5% sodium sulphite solution. It was washed with water again, distilled and re-fluxed over cleaned mercury. It was finally dried with anhydrous calcium sulphate and fractionally distilled; the middle 50% distilling at 77° being retained.

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 to the area of the vessel base, *i.e.* 28.7 cm². The vessels containing 11 ml cleaned mercury and the organic solution were immersed in a stirred paraffin bath thermostatted to ±0.1° by a bimetallic strip (Sunvic Controls Ltd.). After at least 15 min 25 ml 0.1 mole l^{-1} diphenylmercury solution was pipetted into the mercury vessel. 4 ml samples were then removed by pipette from the organic layer at intervals and the count rate measured in 10 ml vials with a NaI(Tl) scintillation counter. The samples were completely free of any colloidal mercury.

RESULTS

Formation of phenylmercuric chloride

A 0.1 mole l^{-1} diphenylmercury solution in carbon tetrachloride was left in contact with static metallic mercury at 55° for 72 hours. A white crystalline precipitate formed in the solution which was centrifuged off and recrystallised from carbon tetrachloride and from 80–100° petroleum ether. The melting point of the dried product was found to be 250–251° (reported[7] for phenylmercuric chloride 251°). A mixed m.p. showed no reduction of this figure. A paper chromatographic separation technique[8] provided a single spot of $R_f = 0.41$ (R_f of phenylmercuric chloride = 0.41; R_f of diphenylmercury = 0.88) and confirmed the identity and purity of the product.

No precipitate was formed in an identical solution of diphenylmercury in carbon tetrachloride nor in a mixture of the same volumes of mercury and carbon tetrachloride when left for similar periods at the same temperature.

Kinetics

The metallic mercury was labelled with [203]Hg and the rate at which the activity transferred to the organic layer was measured by taking aliquots. The activity in the organic layer could have been due to either the exchange of [203]Hg or to the reaction of labelled mercury with diphenylmercury to give labelled phenylmercuric chloride. The final equilibrium value would have been the same in either case and

was calculated from the specific activity of the metal. The activity of the aliquot therefore indicated the extent of the exchange or of the reaction: this was expressed as a percentage.

Plots of percentage reaction against time were straight lines as only a small percentage of the reaction was observed. The slope of this line yielded a value for the rate of the reaction (R in units of mole·sec^{-1}), i.e.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{R(a+b)}{a \cdot b}(x_\infty - x)$$

where x is the activity of tracer in one form at time t (sec), and x_∞ is the activity after infinite time and a and b are the masses in moles of the two substances[9]. If $b \gg a$ and $x \ll x_\infty$ then:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \frac{R}{a}$$

where F is the fraction and $100F$ is the percentage of reaction. The former condition is satisfied because mercury/diphenylmercury is approximately 300/1 and the latter because the slope of the line at zero time is taken. Data for the calculation of the rate at 65.0° are given in Table 1.

In case the formation of phenylmercuric chloride was affected by impurities such as carbon disulphide in the carbon tetrachloride[10], a very thorough purification

TABLE 1

RATE OF REACTION AT 65.0°

Time (min)	Percentage reaction	Rate (10^{-9}·mole·sec^{-1})
Before purification		
5.0	0.14	9.13
13.0	0.27	
21.0	0.47	
30.5	0.68	
14.0	0.26	7.79
29.0	0.56	
44.0	0.76	
59.0	1.12	
After purification		
15.0	0.33	9.12
30.0	0.75	
46.5	1.02	
63.0	1.33	
15.0	0.36	8.68
30.0	0.60	
48.0	0.98	
64.0	1.36	

TABLE 2

ACTIVATION PARAMETERS

Temp. (°C)	Rate (10^{-9}·mole·sec^{-1})
55.0	5.17
60.0	6.86
65.0	8.68
70.0	11.8
76.2	16.6
$\Delta H^* \approx 11.9$ kcal·mole^{-1}	
$\Delta S^* = -66.9$ cal·deg^{-1}·mole^{-1}	
$\Delta G^* \approx 34.5$ kcal·mole^{-1}	

of the solvent was carried out (see Experimental Section). However the solid was still formed and the rate of the reaction was unchanged (Table 1).

The rates of reaction were determined at five different temperatures and the activation parameters determined in the usual manner[11] (Table 2).

Many of the aliquots taken during the kinetic analyses developed crystalline precipitates on cooling: these being greater in mass when a greater percentage of the reaction had been completed. In the kinetic run at 76.2°, the second, third and fourth aliquots all had precipitates when cooled to room temperature. These were centrifuged off, washed with cold carbon tetrachloride, dried and weighed.

The concentration of a saturated solution of phenylmercuric chloride in carbon tetrachloride at room temperature was found to be 0.0196% w/v. Thus a 4 ml aliquot as taken above would have contained an additional 0.0008 g phenylmercuric chloride in solution.

If the activity of the organic layer is due only to radioactive phenylmercuric chloride, then the expected weight of this compound in the 4 ml aliquots can be calculated. Table 3 compares these figures with the total weights found.
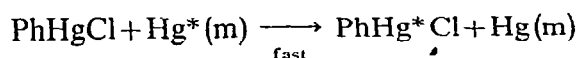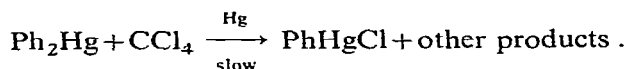
TABLE 3

FORMATION OF PHENYLMERCURIC CHLORIDE

Time (min)	Wt. of ppt. (mg)	Total wt. of PhHgCl (mg)	
		Observed	Calcd.
15.0		0.8	0.7
30.0	1.3	2.1	1.7
44.0	1.8	2.6	2.6
55.0	2.7	3.5	3.6

DISCUSSION

Formation of phenylmercuric chloride by this reaction without doubt requires the presence of diphenylmercury, carbon tetrachloride and mercury. However the similarity between the rate of formation of phenylmercuric chloride and the rate
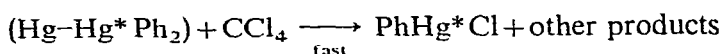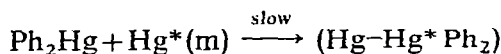
of transference of activity from the mercury to the organic layer (Table 3) limits the possible mechanisms:

(1). Phenylmercuric chloride is formed by reaction of carbon tetrachloride with diphenylmercury upon a mercury surface in a process not involving the exchange of mercury from the metallic layer. The phenylmercuric chloride then exchanges rapidly with metallic mercury.

$$Ph_2Hg + CCl_4 \xrightarrow[\text{slow}]{\text{Hg}} PhHgCl + \text{other products}.$$

$$PhHgCl + Hg^*(m) \xrightarrow[\text{fast}]{} PhHg^*Cl + Hg(m)$$

The rate for the phenylmercuric chloride–mercury exchange in carbon tetrachloride is unfortunately not known. However phenylmercuric chloride exchanges virtually instantaneously with diphenylmercury in a number of solvents at room temperature[12]. If both the homogeneous and the heterogeneous exchanges of phenylmercuric chloride are rapid, the plot of percentage exchange versus time would have shown an upward curve, which was not the case.

(2). Diphenylmercury exchanges with metallic mercury and in the process there is a reaction leading to phenylmercuric chloride.

$$Ph_2Hg + Hg^*(m) \xrightarrow[]{slow} (Hg-Hg^*Ph_2)$$

$$(Hg-Hg^*Ph_2) + CCl_4 \xrightarrow[\text{fast}]{} PhHg^*Cl + \text{other products}$$

where $(Hg-Hg^*Ph_2)$ represents a transition state in the diphenylmercury exchange.

This latter mechanism is in agreement with our conclusions concerning the exchange of diphenylmercury in a series of solvents[3]. We concluded that there was a difference in solvation between the transition state and the ground state. In this case, coordination of a single chlorine atom of carbon tetrachloride would produce sp^2 (trigonal) hybridisation of the mercury atom or coordination of two chlorine atoms would provide sp^3 (tetrahedral) hybridisation. Both structures would be favoured by bending of the linear molecule or any increase in the positive charge on the mercury atom. An S_Ei transition state was postulated for the exchange and this would provide both features. However solvent interaction with carbon tetrachloride becomes so strong that a permanent Hg–Cl bond is formed.

The free energy, enthalpy and entropy of activation are also comparable to the exchange parameters. The free energies of activation for the diphenylmercury exchange in six different solvents[3] varied from 32.2 $kcal \cdot mole^{-1}$ in benzene to 34.6 $kcal \cdot mole^{-1}$ in pyridine. The value for the carbon tetrachloride reaction is remarkably similar. The enthalpies varied from 9.2 $kcal \cdot mole^{-1}$ in toluene to 17.9 $kcal \cdot mole^{-1}$ in benzene and entropies from -42.4 $cal \cdot deg^{-1}$ in benzene to -72.2 in p-xylene. Again the carbon tetrachloride reaction parameters fall in a comparable range.

REFERENCES

1 O. A. REUTOV AND G. M. OSTAPCHUK, *Dokl. Akad. Nauk SSSR*, 117 (1957) 826.
2 D. R. POLLARD AND J. V. WESTWOOD, *J. Amer. Chem. Soc.*, 87 (1965) 2809; D. R. POLLARD AND J. V. WESTWOOD, *J. Amer. Chem. Soc.*, 88 (1966) 1404; M. M. KREEVOY AND E. A. WALTER, *J. Amer. Chem. Soc.*, 89 (1967) 2986.
3 R. A. G. MARSHALL AND D. R. POLLARD, *J. Amer. Chem. Soc.*, in press.
4 G. A. RAZUVAEV AND N. S. VAILEISKAYA, *Dokl. Akad. Nauk SSSR*, 80 (1951) 69.
  O. A. REUTOV, *Fundamentals of Theoretical Organic Chemistry*, North Holland Publishing Co., Amsterdam, 1967.
5 A. E. BORISOV, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1951) 524; A. N. NESMEYANOV, A. E. BORISOV, A. I. KOUREDOV AND E. I. GOLUBEVA, *Tetrahedron*, 18 (1962) 683; L. G. MAKAROVA AND A. N. NESMEYANOV, *The Organic Compounds of Mercury*, North Holland Publishing Co., Amsterdam, 1967.
6 J. H. MATHEWS, *J. Amer. Chem. Soc.*, 48 (1926) 562.
7 F. C. WHITMORE, *Organic Compounds of Mercury*, Chemical Catalogue Co. Inc., Reinhold, New York, N.Y., 1921.
8 J. N. BARTLETT AND G. E. CURTIS, *Anal. Chem.*, 34 (1962) 80.
9 A. C. WAHL AND N. A. BONNER, *Radioactivity applied to Chemistry*, Wiley, New York, N.Y., 1951, p. 34.
10 A. WEISSBERGER, E. S. PROSKAUER, J. A. RIDDICK AND E. E. TOOPS, *Organic Solvents*, Interscience, New York, N.Y., 2nd ed., 1955, p. 413.
11 S. GLASSTONE, K. J. LAIDLER AND H. EYRING, *The Theory of Rate Processes*, McGraw-Hill, New York, N.Y., 1941, p. 197.
12 M. H. THOMPSON, *A Kinetic and Mechanistic Investigation into Isotope Exchange Reactions of Some Diaryl Mercury Compounds*, Ph.D. thesis, University of London, 1970.