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

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*Contribution from the Department of Chemistry, Sir John Cass College, London, England. Received December 12, 1964*

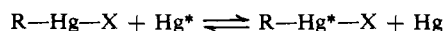
*A kinetic study has been made of exchange between a stirred metallic mercury surface and diphenylmercury in solution. Results indicate that with careful selection of experimental conditions, diffusion control is avoided. Reaction has been shown to occur reproducibly, reversibly, and heterogeneously without complexity of products, and with a rate directly dependent on the mercury surface area. Anomalous mercury aryl concentration effects are explained in terms of inhibition by reaction product.*

### Introduction

In recent years mercury organic compounds have been of interest owing to their application to the study of electrophilic substitution. In particular, Nesmeyanov and Reutov<sup>2</sup> and Ingold<sup>3</sup> have made detailed investigations of homogeneous mercury aryl exchange reactions and proposed mechanisms for electrophilic substitution analogous to the well-characterized nucleophilic types.

Few workers have considered heterogeneous exchange reactions quantitatively, mainly owing to experimental difficulties in dealing with large uniform surface areas under controlled conditions. Haissinsky<sup>4</sup> first used a tagged metallic mercury layer to investigate exchange with inorganic mercury compounds in aqueous solution. He concluded diffusion control but did not attempt a rigorous kinetic investigation.

We noted that reactions involving the homogeneous decomposition of mercury aryl compounds in solution proceeded faster following the appearance of metallic mercury droplets. A similar effect was reported by Reutov.<sup>5</sup> Reutov and Ostapchuk<sup>6</sup> and Reutov and Yan-tsei<sup>7</sup> have reported the exchange of mercury organic compounds with a stirred metallic mercury layer.



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

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

(3) C. K. Ingold, *J. Chem. Soc.*, 2523 (1959).

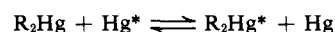
(4) M. Haissinsky and M. Cottin, *J. chim. phys.*, 45, 224 (1948); 46, 476 (1949).

(5) O. A. Reutov, *Tr. Inst. Fiz. Khim. Akad. Nauk SSSR* 22, 3315 (1951).

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

(7) O. A. Reutov and U. Yan-tsei, *ibid.*, 117, 1003 (1957).

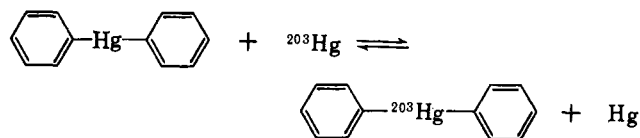
and



They produced evidence to show that free radicals were not involved but omitted the rigorous kinetic data needed for quantitative analysis of the reaction mechanism.

To account for the observed dipole moment, Hampson<sup>8</sup> suggested that mercury organic compounds were not strictly linear "sp" hybrids in solution. Dessy and Kim<sup>9</sup> have invoked nonlinearity to account for reactions with HCl. More direct evidence has been given by Schneider and Buckingham,<sup>10</sup> who showed large chemical shifts (82 p.p.m.) by n.m.r. studies when  $Hg(CH_3)_2$  was diluted with pyridine and attributed this to changes of hybridization by solvent coordination. Similar effects in mercury aryl molecules require investigation. It was hoped that heterogeneous exchange reactions might provide further evidence, as molecular orientation effects may be involved in any adsorption process.

This paper is mainly concerned with the establishment of experimental techniques and factors affecting the exchange



prior to a systematic kinetic investigation of possible mechanisms of exchange for diphenylmercury and its symmetrically monosubstituted derivatives.

### Experimental

1. *Materials.* Diphenylmercury was prepared from bromobenzene in xylene solution by the sodium amalgam method,<sup>11</sup> with ethyl acetate as catalyst, and purified by double recrystallization from benzene (m.p. 123–124°; lit. m.p. 122°, 125–126°<sup>13</sup>). Di-*o*-tolylmercury was prepared by converting *o*-bromobenzene to the Grignard reagent and treating it with mercuric chloride in ether–benzene solution. Purification was effected

(8) G. C. Hampson, *Trans. Faraday Soc.*, 30, 877 (1934).

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

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

(11) E. Dreher and R. Otto, *Ber.*, 2, 542 (1869).

(12) E. Dreher and R. Otto, *Chem. Zentr.*, 2, 822 (1912).

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

by crystallization from benzene (m.p. 100–101°, lit.<sup>14</sup> m.p. 106.5–107°). Di-*p*-tolylmercury was prepared by the sodium amalgam synthesis from *p*-bromotoluene and crystallized from benzene (m.p. 243°, lit.<sup>15</sup> 238°). *p*-Tolylphenylmercury was prepared from 2 mole equiv. of phenylmagnesium bromide and 1 mole equiv. of *p*-tolylmercuric chloride. The temperature was kept below 10° (dec. pt. 122°, lit.<sup>16</sup> dec. pt. 120°).

Radioactive diphenylmercury containing mercury labeled with <sup>203</sup>Hg was prepared from active mercuric chloride and diazotized aniline hydrochloride by the method of Nesmeyanov.<sup>17</sup> Active mercuric chloride was prepared from 1 g. of mercury metal containing 500  $\mu$ curies of <sup>203</sup>Hg. All stages of preparation were carried out on a sintered glass plate using apparatus similar to that of Carson, Stranks, and Wilmshurst<sup>18</sup> (m.p. 125°; lit. m.p. 122°,<sup>12</sup> 125–126°<sup>13</sup>).

Radioactive mercury was produced by irradiation of A.R. mercury in silica ampoules with thermal neutrons in the pile BEPO (Harwell, England). Mercury (1 g.) containing 500  $\mu$ curies of <sup>203</sup>Hg was diluted with inactive mercury to produce a stock solution containing approximately 2–4  $\mu$ curies/100 g. for kinetic use.

Solvents used were purified as follows. Pure and crystalline benzene (Harrington) was dried with sodium wire and fractionally distilled from all-glass apparatus; the fraction boiling at 79–81° was collected<sup>19</sup> for use as the reaction medium.

Analar grade dioxane (M. and B.) was refluxed with solid stannous chloride to remove peroxides and distilled to remove water as the azeotrope.<sup>20a</sup> The fraction boiling from 100.5 to 101.5°, lit.<sup>20b</sup> b.p. 101–103°, was collected for use as the reaction medium and chromatographic eluent. As traces of peroxides caused spurious spots on the chromatograms, the dioxane was stored over solid ferrous sulfate and passed through a long column of alumina prior to use. B.D.H. reagent grade pyridine was converted to the coordination compound with zinc chloride in aqueous hydrochloric acid containing ethanol, decomposed with caustic soda solution, dried over solid caustic soda, and distilled fractionally, collecting the fraction boiling at 114.0–115.0°, lit.<sup>21</sup> b.p. 114.5°, for use as kinetic solvent and counting medium.

2. *Analytical Procedure.* (a) *The Labeling Isotope.* Choice of the labeling isotope fell on <sup>203</sup>Hg owing to its simple decay scheme and long half-life ( $t_{1/2} = 47.0$  days). This was produced by ( $n, \gamma$ ) reaction from <sup>202</sup>Hg. Owing to the high absorption cross section of <sup>196</sup>Hg ( $\sigma = 2500$  barns) as compared with <sup>202</sup>Hg ( $\sigma = 3.8$  barns), a larger proportion of activity due to <sup>197</sup>Hg and <sup>197m</sup>Hg was present after irradiation than due to <sup>203</sup>Hg, in spite of the smaller natural abundance of <sup>196</sup>Hg. Storage for a period of 42 days was found to reduce the activity of

<sup>197</sup>Hg to less than 0.5% of the total. A half-life plot after this period confirmed that the remaining activity was due to <sup>203</sup>Hg only.

<sup>203</sup>Hg is a ( $\beta^-$ ,  $\gamma$ ) emitter of fairly low energy ( $E_{\beta_{max}} = 0.208$  Mev.,  $E_{\gamma} = 0.279$  Mev.). It is considered to be best counted as a  $\gamma$ -emitter, and this was confirmed with the equipment available by relative efficiency measurements and statistical tests.<sup>22</sup> From these it was clear that the well-type scintillation counter was the most effective. A scintillation counter Type USC/B (manufactured by Panax Equipment Ltd.) was used for all kinetic studies. This counter uses as detector a  $2 \times 1.75$  in. thallium-activated sodium iodide crystal with a  $0.75 \times 1.25$  in. well (Hilger and Watts), and a single 11-stage photomultiplier tube (E.M.I. 6097B), with extra high tension (E.H.T.) supplied by a high stability power unit. This was contained in a lead castle providing a minimum of 1-in. shielding in all directions. The output of the photomultiplier tube was connected to a linear pulse amplifier and then fed into a scaling unit (Panax Type 100S) incorporating an electronic timer and a voltage discriminator variable from 5 to 50 v. Liquid samples were counted in clinical vial-type polythene-capped glass bottles holding a maximum of 8 ml. of solution. These were a loose fit in the well of the detector. To keep well within the active volume of the crystal, samples were restricted to a maximum volume of 4 ml.

Counter operating conditions were arrived at by a careful selection of the variables E.H.T., amplifier gain, and discriminator bias, so as to count under plateau conditions and maintain maximum signal-to-noise ratio. Methods of visual inspection and confirmation by a statistical method<sup>22</sup> were used to obtain the optimum values of these parameters from the characteristic curves for sample and background. An E.H.T. voltage of 1200 v. and discriminator bias of 18 v. were used. The slope of the count rate/E.H.T. characteristic was 1.2%/100 v., and the plateau length was 250 v., which was considered very satisfactory. Sufficient discriminator voltage was used to cut off pulses from  $\beta$ -radiation and electronic noise while remaining under plateau conditions. Counter performance was checked prior to use with a reference source of 3 ml. of <sup>137</sup>Cs solution sealed into a glass vial. This gave a counting efficiency for <sup>137</sup>Cs of 48%. A stabilization time of 40 days allowed the phosphor to lose its long term luminescence after assembly; measurements were made only after this period, and the counter was not opened until all measurements were completed. The correlation coefficient for a count rate/volume of active solution plot was 0.997, establishing linearity of response over the range required.

(b) *Reaction Procedure.* Choice of reaction vessels was based on design simplicity, ease of replacement on breakage, and reproducibility of geometry between vessels (Figure 1). The stirrer was made from borosilicate glass to be a good fit in the gland, and in the simplest possible reproducible shape. The reaction vessels were immersed in an electrically heated oil bath, thermostated by a mercury-toluene regulator with a temperature stability of  $\pm 0.1^\circ$  up to 95°. All kinetic runs were performed in duplicate.

(22) K. D. Outeridge, "The Statistics and Comparison of Counters," Atomic Energy Research Establishment Memorandum 1/M 32, Harwell, Berks, 1954.

(14) F. C. Whitmore and R. J. Sobatski, *J. Am. Chem. Soc.*, **55**, 1128 (1933).

(15) E. Dreher and R. Otto, *Ann.*, **154**, 171 (1870).

(16) M. S. Kharasch and R. Marker, *J. Am. Chem. Soc.*, **48**, 3130 (1926).

(17) A. N. Nesmeyanov, *Ber.*, **62**, 1010 (1926).

(18) A. S. Carson, D. R. Stranks, and B. R. Wilmshurst, "Radioisotopes in Scientific Research," Vol. II, Proceedings of the 1st U.N.E.-S.C.O. International Conference, 1957, p. 447.

(19) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1959, p. 172.

(20) A. Weissberger, "Organic Solvents," 2nd Ed., Interscience Publishers Inc., New York, N. Y., 1955: (a) p. 318; (b) p. 371.

(21) Reference 20, p. 175.

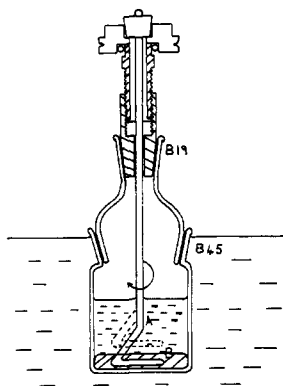


Figure 1. Reaction vessel for mercury exchange.

Mercury was weighed out to within  $\pm 0.01$  g. of the required quantity by means of a special pipet,<sup>23</sup> added to the lower dry part of the vessels, and equilibrated in the thermostat for 5 min. A portion (20 ml.) of the mercury aryl solution used was added by piston pipet. The upper parts of the vessels and stirrers were assembled to the required geometry (Figure 1) and stirring commenced at the required speed. Sealing of vessel and starting of stirrer occupied less than 15 sec., *i.e.*, less than 1% of the shortest reaction period. Stirring was checked periodically for stability against a stroboscopic standard (Dowe Strobflash Type 1200D) and could be maintained constant to  $\pm 20$  r.p.m. over the period of a run.

Sampling of a single vessel was first attempted as reported in the initial Russian papers.<sup>6,7</sup> This led to anomalous results as the relative molar composition of the two phases changed each time a sample was taken (Figure 2), and therefore the following procedure was adopted.

A series of four or five vessels was used for different times on each kinetic run. On completion of the reaction period the mercury aryl compound solution was gray in color and was passed through a 3-in. column of alumina, from which it emerged colorless. The coloration was due to a fine suspension of mercury. This was confirmed by a kinetic run for 4 hr. at 75° using 75 g. of mercury containing 25  $\mu$ curies of <sup>203</sup>Hg and 20 ml. of benzene containing 0.3 g. of diphenylmercury. Stirring was carried out with the stirrer in position B (Figure 1) at 1400 r.p.m. After reaction the benzene layer was decanted, and on standing a fine gray precipitate settled. Benzene was removed and the residue washed with additional benzene and dried. On rubbing gently the powder coalesced into the characteristic shiny globules of mercury. A portion of it was weighed and dissolved in concentrated nitric acid and gave an average corrected count rate compared with a sample of the original active mercury metal treated similarly as shown: original mercury, 14,915 counts/sec./g.; Gray precipitate, 14,995 counts/sec./g. Reutov<sup>6</sup> suggested precipitating the mercury aryl compound with petroleum ether after sampling, but in our experiments this resulted only in partial precipitation; therefore, the following procedure was adopted. Benzene was evaporated off under a heat lamp in a stream of dry air, and to a portion of the residue (*ca.* 0.3 g.), accurately

(23) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1958, p. 781.

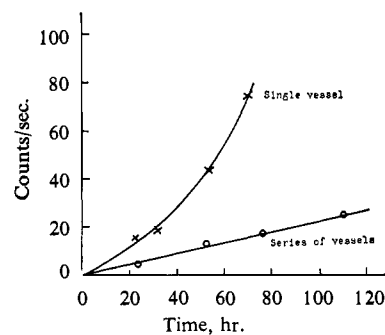


Figure 2. A comparison of sampling methods.

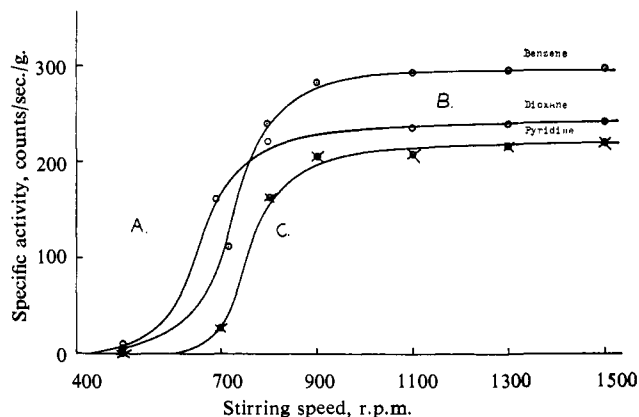


Figure 3. The variation of exchange with stirring speed.

weighed into a counting vial, 4 ml. of pyridine was added and the vial sealed for counting.

## Results

**1. Stirring.** In past investigations of similar heterogeneous processes,<sup>4,7</sup> stirring speeds appear to have been somewhat arbitrarily selected. It was important to eliminate by stirring diffusion effects in the mercury and mercury aryl solution layers. Therefore the effect on the reaction of stirring speed was studied in detail. The stirrer was used in position B (Figure 1). Owing to the small percentage of the total reaction observed in a reasonable time, it was inconvenient to measure the exchange fraction. Thus results were obtained in terms of specific activity (counts/sec./g.) after 2-hr. exchange for a series of stirring speeds. Portions (20 ml.) of diphenylmercury (0.155 mole/l.) in benzene, dioxane, or pyridine were taken and run at  $70.0 \pm 0.1^\circ$  with  $75.00 \pm 0.01$  g. of mercury metal. Results are shown in Figure 3. The curves show three distinct regions.

In region A it was observed that stirring was insufficient to break up the mercury pool. To investigate this region more fully, exchange was performed over a still mercury surface with sufficient stirring to maintain mercury aryl solution composition uniform without agitation of the mercury pool (*i.e.*, 100 r.p.m. in position A, Figure 1). Results for diphenylmercury show that the specific activity increase per hour was constant at  $0.215 \pm 0.003$  count/sec./g. at 45°, 0.155 *M* (five measurements between 23.5 and 100.0 hr.);  $0.210 \pm 0.002$  count/sec./g. at 45°, 0.291 *M* (five measurements between 23.5 and 110 hr.); and  $0.248 \pm 0.007$  count/sec./g. at 75°, 0.115 *M* (five measurements between 23.5 and 110 hr.). Similar results were obtained for di-*o*-tolylmercury. Tagged metallic mercury (75 g.) was

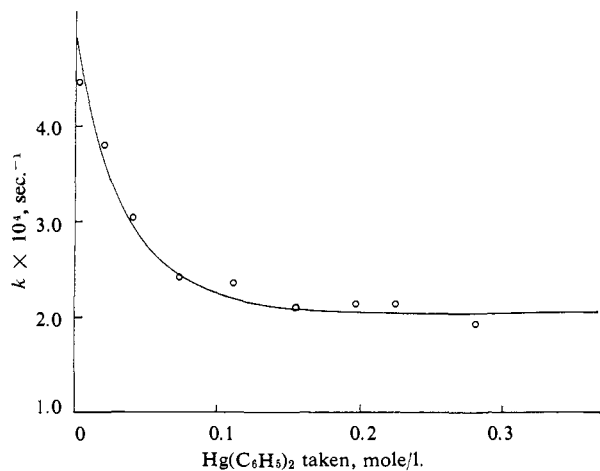


Figure 4. Variation of rate constant with aryl concentration.

taken for each run and 25 ml. of aryl solution. Diffusion control within the mercury layer was assumed.

In region B it was observed that within 30 sec. of starting the stirrer, all the mercury was split into small droplets.<sup>4</sup> The dramatic increase in reaction rate may be attributed to the breakdown of diffusion control by sufficient stirring. A more detailed kinetic investigation in this region was therefore possible and is reported in this and subsequent papers. In all following experiments, stirring was maintained at  $1400 \pm 20$  r.p.m. in position B (Figure 1), *i.e.*, well on the plateau of Figure 3.

Region C is the region of change over from diffusion to exchange control and corresponds practically to the region of formation of mercury droplets. The position of this region on the stirring speed axis depends on the stirring efficiency, *i.e.*, on the vessel and stirrer geometry, which should be specified for heterogeneous exchanges.

2. *Identification of Reaction Products.* Reutov and Ostapchuk<sup>6</sup> report that on carrying out the reaction with (*p*-nitrophenyl)phenylmercury, no products other than the starting materials could be isolated. This work was confirmed using a sensitive ascending paper chromatographic technique by Bartlett and Curtis<sup>24</sup> to identify products. This was not in existence at the time of the Russian work.

The method was shown to be sensitive to amounts of mercury less than 1  $\mu$ g. in each spot. The reaction was performed using the usual method, at 45° for 6 hr., with a 0.05 *M* solution of *p*-tolylphenylmercury in benzene. A portion of the resulting solution was chromatographed and yielded only one spot ( $R_f$  0.77) corresponding to *p*-tolylphenylmercury ( $R_f$  0.76), as compared with diphenylmercury ( $R_f$  0.89) and di-*p*-tolylmercury ( $R_f$  0.72).

3. *Evaluation of Kinetics.* It is usual to interpret the kinetics of exchange processes in terms of a plot of  $-\ln(1-F)$  vs.  $t$ , where  $F$  is the fraction of exchange occurring in time  $t$ , *i.e.*,  $S_t/S_\infty$ , where  $S$  is specific activity. All reactions investigated gave a linear plot of  $-\ln(1-F)$  vs.  $t$ ; thus the process was first order following an expression

$$kt = -\ln(1-F)$$

where  $k$  (sec.<sup>-1</sup>) is a rate constant.

(24) J. N. Bartlett and G. W. Curtis, *Anal. Chem.*, **34**, 80 (1962).

Table I. Reproducibility of Experimental Method

| Aryl soln., mole/l. | Temp., °C. ( $\pm 0.1$ ) | No. of replicates |          |          |
|---------------------|--------------------------|-------------------|----------|----------|
|                     |                          |                   | <i>a</i> | <i>b</i> |
| 0.020               | 70.0                     | 5                 | 15       | 5        |
| 0.160               | 70.0                     | 5                 | 12       | 5        |
| 0.160               | 40.0                     | 6                 | 13       | 7        |

<sup>a</sup> Maximum spread per cent of replicate points on  $-\ln(1-F)$  vs.  $t$  plot. <sup>b</sup> Maximum spread per cent of replicate slopes on  $-\ln(1-F)$  vs.  $t$  plot.

Practical difficulties arise where, as in this case,  $S_\infty$  must be found by extrapolation from an exponential plot of  $S_t$  vs.  $t$ . Guggenheim<sup>25</sup> and Smith<sup>26</sup> have reviewed methods of obtaining  $S_\infty$  values and have shown that for a first-order process

$$S_\infty = S_1 + \frac{(S_2 - S_1)^2}{2S_2 - S_1 - S_3}$$

where  $S_1$ ,  $S_2$ , and  $S_3$  are specific activities taken such that  $(t_2 - t_1) = (t_3 - t_2)$ . This formula is no more accurate than the least accurate of its readings; however, it constituted a reasonable method for finding  $S_\infty$ , as it is doubtful whether a visual extrapolation could even approach this accuracy. Repeated application of this formula has been used to determine  $S_\infty$  values throughout this and subsequent investigations.

4. *Reproducibility.* Replicate experiments were performed under the usual conditions in order to assess the reproducibility of the results obtained. These are summarized in Table I. These values were considered very satisfactory in view of the heterogeneous nature of the process and compare well with similar results obtained by other workers.<sup>4,7</sup>

5. *Quantitative Recovery of Mercury Aryl.* It is well known<sup>27</sup> that mercury aryl compounds in solution undergo decomposition on heating to metallic mercury. Replicate experiments were performed to establish whether this process was of importance over the time and temperature range taken for these reactions: weight of mercury,  $75.00 \pm 0.01$  g.; aryl solution, 20 ml. of 0.035 *M* diphenylmercury in benzene; temperature,  $75.0 \pm 0.1^\circ$ ; time of run, 4.5 hr. The highest recorded loss in three experiments was 0.6 mg. (0.24%), indicating that any decomposition was negligible.

6. *Effect of Varying Concentration.* Dependence of the rate constant on mercury aryl compound concentration was investigated using the experimental procedure detailed above.  $k$  was obtained for a series of mercury aryl concentrations. Conditions were  $75.00 \pm 0.01$  g. of mercury; aryl solution, 20 ml. of diphenylmercury in benzene; temperature,  $70.0 \pm 0.1^\circ$ . Results are presented in Figure 4.

Owing to the unusual increase of reaction rate with decreasing concentration, it would have been best to use a working concentration for future experiments in excess of 0.1 mole/l., *i.e.*, in the plateau region. However, the more substituted mercury aryls (part II of this series) were not soluble to this extent, and to ensure consistency of results, 0.05 mole/l. was selected as the most practical.

(25) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

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

(27) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalogue Co. Inc., Reinhold Publishing Corp., New York, N. Y., 1921, p. 361.

Table II. The Effect of Dissolved Mercury on the Reaction

| Kinetic run         | Temp., °C. (±0.1) | Time of run, hr. | Wt. of Hg, g. (±0.01) | Total counts, sec. |
|---------------------|-------------------|------------------|-----------------------|--------------------|
| Benzene (20 ml.)    | 55.2              | 4.5              | 75.00                 | 0.26               |
| Blank               | ..                | ..               | ..                    | 0.24               |
| Sample of tagged Hg | ..                | ..               | 0.2314                | 84.86              |

Table III. Activation Parameters

| Temp., °K.                  | $k \times 10^4$ , sec. <sup>-1</sup> | Log PZ                      |
|-----------------------------|--------------------------------------|-----------------------------|
| Diphenylmercury             |                                      |                             |
| 343                         | 2.10                                 | 5.467                       |
| 333                         | 1.42                                 | 5.571                       |
| 328                         | 0.57                                 | 5.319                       |
| 323                         | 0.38                                 | 5.294                       |
| 313                         | 0.27                                 | 5.451                       |
| 303                         | 0.14                                 | 5.505                       |
| Radioactive Diphenylmercury |                                      |                             |
| 343                         | 2.04                                 | 5.631                       |
| 333                         | 1.49                                 | 6.180                       |
| 323                         | 0.49                                 | 5.554                       |
|                             | Inactive diphenylmercury             | Radioactive diphenylmercury |
| $E_a$ , kcal./mole          | 14.3                                 | 14.6                        |
| $\Delta F^*$ , kcal.        | 25.3                                 | 25.3                        |
| $\Delta H^*$ , kcal.        | 13.6                                 | 14.0                        |
| $-\Delta S^*$ , e.u.        | 35.1                                 | 33.9                        |

Dependence of rate constant on the quantity of metallic mercury taken per run was investigated in a similar manner. The conditions were: aryl solution, 20 ml. of 0.035 M diphenylmercury in benzene; temperature, 70.0 ± 0.1°. Kinetic runs were repeated for increasing amounts of metallic mercury. The results are recorded in Figure 5.

7. *Effect of Dissolved Mercury.* Reports<sup>28,29</sup> suggest that the solubility of metallic mercury in benzene is appreciable. To establish whether the reaction might be in whole or in part homogeneous, experiments were carried out to detect dissolved mercury. Kinetic runs were carried out as previously detailed using 20 ml. of benzene containing no dissolved mercury aryl compound and 75 g. of metallic mercury per run. The benzene samples were passed through a glass wool plug to remove suspended particles and concentrated to 4 ml. in the counting vials. Typical results are shown in Table II. Thus the amount of dissolved mercury is not likely to be significant in the present investigation.

8. *Activation Parameters of Diphenylmercury and Reversibility.* Using the above experimental technique, a plot of  $-\log(1 - F)$  vs.  $t$  was made for a series of temperatures, and activation parameters were deduced from the usual thermodynamic equations.<sup>30</sup> Results are presented in Table III.

To test whether the reaction was reversible, kinetic runs were made with a layer of nonlabeled mercury

(28) A. C. Moser and A. F. Voigt, *J. Am. Chem. Soc.*, **79**, 1837 (1957).

(29) H. Reichart and K. F. Bonhoeffer, *Z. Physik*, **67**, 780 (1931).

(30) 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.

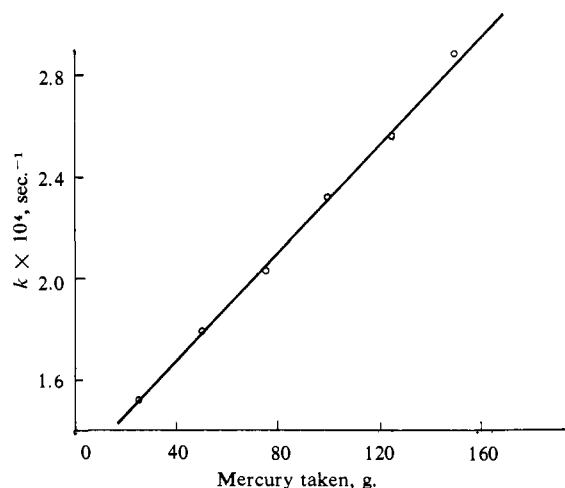


Figure 5. The variation of rate constant with mercury taken.

metal and radioactive diphenylmercury. Owing to preparative difficulties of radioactive diphenylmercury, only three kinetic runs were possible; however, activation parameters show good agreement with those for the inactive compound.

9. *Adsorption Effects.* Reaction must take place following adsorption of the mercury aryl compound from solution onto the surface. To demonstrate directly that adsorption effects were involved, the reaction was repeated as before, using diphenylmercury with added quantities of organic compounds known to possess surface active properties. With lauryl alcohol (0.028 mole/l.) at 328°K., the rate constant  $K$  was  $4.32 \times 10^{-4}$  sec.<sup>-1</sup>; similarly with camphor (0.017 mole/l.) at 328°K., the rate constant was  $3.35 \times 10^{-4}$  sec.<sup>-1</sup>.

A comparison with Table III shows that in both cases a considerably increased rate was observed. The mercury layer was split into very fine droplets, much finer than in previous experiments. It was established by separate blank experiments (containing no dissolved diphenylmercury) that the added surface active agents did not react chemically with the mercury layer to produce soluble products which could contribute to the specific activity recorded in the aryl compound following exchange.

### Discussion

Moelwyn-Hughes<sup>31</sup> argues that no kinetic interpretation of heterogeneous processes is possible unless (a) the two solvents are immiscible and nonemulsifiable; (b) each reactant is soluble in one phase only; (c) the products are soluble in at least one phase; and (d) no factors disturb the surface conditions, other than those involved in reaction. These conditions appear to be satisfied in the present study.

Sampling of a single reaction vessel only presents a true picture if the mercury-mercury aryl solution layer exists as a homogeneous suspension at the time of sampling, when equivalent quantities of mercury and mercury aryl solution are removed in the sample. This was not true under still surface conditions; neither did it become a sufficiently good approximation with vigorous agitation. To be comparable, successive runs must duplicate not only concentration but also the proportion of the total volume occupied by each phase.

(31) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1933, p. 291.

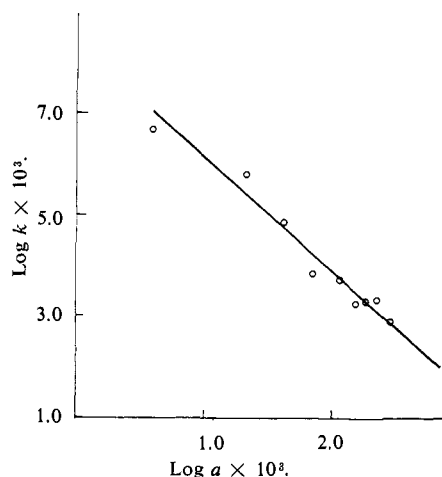


Figure 6. Freundlich isotherm plot.

For still surface exchanges, the low rate could be due to two factors: first, that the surface area available for reaction was small (*ca.* 53 cm.<sup>2</sup>); second, that the process was diffusion controlled. Sufficient stirring was always maintained to ensure that diffusion was not of importance in the aryl solution, but it is reasonable to suppose that after an initially rapid exchange with the solution, the concentration of active mercury in the Hg surface could only be maintained by self-diffusion from the bulk, which would then be rate determining. Though no accurate estimate of activation energy could be made, a value of less than 5 kcal. in each example is consistent with the results and diffusion control (*cf.* Haissinsky,<sup>4</sup> 3.2 kcal.).

In region B (Figure 3) all mercury was present in the form of small drops. It seems reasonable to ascribe the small rise in the plateau region to the decrease of drop size and increase of surface area with stirring speed. However, the rise is small and justifies a working speed on this plateau with a possible variation of  $\pm 200$  r.p.m. without serious change of rate.

For a simple bimolecular reversible isotopic exchange process in a homogeneous stable system the relation<sup>32</sup>

$$Rt = \frac{ab}{a\beta + b\alpha} \ln(1 - F) \quad (1)$$

will follow where  $a$  = the concentration of radioactive <sup>203</sup>Hg plus inactive Hg in the mercury aryl layer;  $b$  = the concentration of radioactive <sup>203</sup>Hg plus inactive Hg in the metallic mercury layer;  $\alpha$  and  $\beta$  = kinetic isotope effects in the two opposing transfer directions constituting the exchange equilibrium. Here these are unity and  $b \gg a$ ; hence

$$k't = -\ln(1 - F) \quad (2)$$

where  $k'$  (sec.<sup>-1</sup>) is a pseudo-first-order rate constant. These equations have equal applicability to heterogeneous processes,<sup>33,34</sup> provided that diffusion does not form a concentration gradient of labeled material. It has been shown practically that the reaction is reversible, diffusion effects may be rendered insignificant, and also a relation similar to eq. 2 is obeyed. Thus taking a typical exchange, *e.g.*, Hg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> at 50° (Table III),  $a = 7 \times 10^{-4}$  mole (*e.g.*, in 0.25 g. of Hg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>) and  $b = 4 \times 10^{-1}$  mole (75 g. of metallic mercury) (*i.e.*,  $b \gg$

(32) H. McKay, *Nature*, **142**, 997 (1938).

(33) T. H. Norris, *J. Phys. Chem.*, **54**, 777 (1950).

(34) R. P. Bell, *ibid.*, **32**, 882 (1928).

$a$ );  $S_{\infty} = 128$  counts/sec./g. for 0.25 g. of aryl taken; and the specific activity of the mercury layer = 250 counts/sec./g. for 75 g. of mercury taken; *i.e.*, during reaction only 0.2% of the activity is removed from the mercury layer. Thus eq. 2 applies.

In view of this first-order relationship, the behavior of the rate constant with changing concentration is at first surprising, as it theoretically should be independent of these factors. Linear dependence of rate constant with mercury excess may be attributed to the corresponding change of mercury surface area. For this heterogeneous process, the Arrhenius equation<sup>35</sup> becomes

$$k = P\bar{n}ce^{-E_a/RT}$$

where  $\bar{n} = W\bar{c}/\Phi_b\sqrt{6\pi}$  = the number of particles/sec. striking a given unit area;  $W$  = the number of particles in a total of  $M$  species (solute and solvent);  $\bar{c}$  = the r.m.s. velocity of a particle;  $\Phi_b$  = the molecular co-volume of the solution; and  $c$  = the surface area. Thus  $k$  is linearly dependent on the surface area. Owing to difficulties of measurement of  $c$ ,  $\bar{n}$  is difficult to evaluate completely. However, it is reasonable to suppose that for a given stirring speed (*i.e.*, mercury drop size) the effect of adding more mercury excess is to increase the reaction surface area. Figure 5 also confirms the fact that the reaction is heterogeneous as, in addition to absence of evidence of significant dissolved mercury, if reaction takes place in solution, addition of further mercury should have no effect, assuming the solution to be saturated. For quantities of mercury less than sufficient to cover the vessel base, it tends to remain as a single drop for an appreciable time. This accounts for the apparent delayed start to the reaction shown in Figure 5.

Variation of rate constant with mercury aryl concentration is more difficult to account for. An explanation is that the mercury aryl molecules must be adsorbed prior to reaction. Adsorption effects may be treated by the Langmuir adsorption isotherm

$$\frac{x}{m} = \frac{k_1k_2a}{1 + k_1a}$$

which reduces to

$$\frac{x}{m} = ca^{1/n}$$

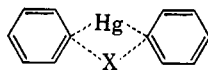
at intermediate values (Freundlich isotherm) of concentration where  $1/n$  lies between 0 and 1. In the region above 0.1 mole/l. (Figure 4), the concentration is high, and  $x/m$  is a constant; *i.e.*, the mercury surface is completely covered with an adsorbed monomolecular layer of aryl mercury molecules. The reaction rate will depend on the amount adsorbed, *i.e.*, a constant. Below 0.1 mole/l. eq. 3 should apply; *i.e.*, the amount of material in true solution is comparable with that adsorbed. From Figure 6,  $1/n = -0.205$ . Numerically this value is reasonable but the sign is unusual. Moelwyn-Hughes<sup>36</sup> has explained such curves in terms of the selective adsorption of the products; *i.e.*, if the product and reactants are highly adsorbable, but the latter more than the former, the rate may become inversely proportional to the concentration of the products which must possess a hybridization state that allows them to be more strongly held on the surface.

(35) S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

(36) Reference 31, p. 267.

The effect of added surface active agents was unexpected. It was anticipated that such active material would be preferentially adsorbed and block adsorption sites leading to a reduced reaction rate, but this was contrary to the observed facts. The mercury droplets produced in these reactions were extremely small; *i.e.*, the surface area (and reaction rate) was increased masking any effect due to the blocking of adsorption centers. Smaller droplets could be ascribed to a strongly held film of the surface active material preventing coalescence. Quantitative interpretation must depend on measurement of surface area involved, preferably using a series of compounds and conditions. A later report on kinetic data for such a series will include the quantitative interpretation of surface area measurements.

Only preliminary observations on the reaction mechanism may be made at this stage. Neither ionic nor free radical mechanisms appear to be involved, as mercury aryl free radicals have only been observed under exceptional conditions.<sup>37</sup> Chromatographic evidence points to a transition state similar to that proposed by Reutov, *i.e.*



where X is some species of mercury atom, the nature of

(37) J. Kraus, *J. Am. Chem. Soc.*, **35**, 1732 (1913).

which is the subject of future work. Five steps in the reaction process are envisaged: (1) transport of the reactants to the surface, (2) adsorption of reactants on to the surface, (3) reaction at the surface, (4) desorption of the products from the surface, and (5) transport of the reactants from the surface.

Steps 1 and 5 would be rate controlling in a diffusion-controlled reaction. In the absence of solvent effects, steps 2 and 4 should require the same activation energy, but anomalous concentration effects suggest that this is not so. It would be expected that the reactants should be solvated, and the products, at least initially, not. Solvation of the arylmercury atom tends to produce an angled  $sp^3$  configuration from the linear  $sp$  type. It must be presumed that the linear structure would be the more strongly adsorbed, leading to the observed inhibition of reaction product. If this theory is correct, then change of solvent should produce little change of reaction rate but change the shape of Figure 4. Also the effect of varying benzene ring substituents should produce a change of rate. In particular, *ortho* substituents might be expected sterically to influence the transition state, and *para* substituents to inhibit the adsorbability of the reactants in the angled structure. These effects may be treated by the Hammett and Leffler relationships and form the subject of the next contribution.

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## A $P^{31}$ Nuclear Magnetic Resonance Study of Complexing between $Li^+$ , $Ca^{2+}$ , and $Mg^{2+}$ Ions and the Lower Condensed Phosphate Polyanions<sup>1</sup>

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*High resolution 24.3-Mc.  $P^{31}$  nuclear magnetic resonance spectra of the aqueous tetramethylammonium salts of several condensed phosphate polyanions—pyrophosphate, tripolyphosphate, trimetaphosphate, and tetrametaphosphate—have been studied as a function of added  $Li^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  chlorides. Complex formation between the added cations and the phosphate anions produces observable changes in the phosphorus chemical shifts and spin coupling constants. The data give information about the stoichiometry, relative strength, mean lifetime, and dynamic structural geometry of the complexes. The concept of specific site binding is discussed in terms of a simple electrostatic model.*

### Introduction

The tendency for strong complex formation in aqueous solution between alkali or alkaline earth

(1) A portion of this paper was presented before the Division of Inorganic Chemistry, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

metal ions and the lower condensed phosphates, particularly pyrophosphate,  $P_2O_7^{4-}$ , and tripolyphosphate,  $P_3O_{10}^{5-}$ , is well known.<sup>1-6</sup> Most studies of these complexes have been concerned with quantitative determinations of their stability constants or with their stoichiometric formulas. There has been considerable speculation as to the nature of the bonding in such complexes, *i.e.*, whether partly covalent or totally ionic in character, and, if ionic, whether or not the cations are bound at specific sites of the polyanion as opposed to a random, nonoriented, ionic-atmosphere type of electrostatic attraction. The physical evidence has been discussed by Van Wazer and Callis.<sup>2</sup>

Calculated Bjerrum radii of metal polyphosphate complexes have been interpreted in favor of ionic

- (2) J. R. Van Wazer and C. F. Callis, *Chem. Rev.*, **58**, 1011 (1958).  
 (3) S. M. Lambert and J. I. Watters, *J. Am. Chem. Soc.*, **79**, 5606 (1957).  
 (4) J. I. Watters and S. M. Lambert, *ibid.*, **81**, 3201 (1959).  
 (5) R. R. Irani and C. F. Callis, *J. Phys. Chem.*, **64**, 1398 (1960).  
 (6) R. R. Irani, *ibid.*, **65**, 1463 (1961).