22. *The Pyrolysis of Organomercury Compounds.*

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The thermal decomposition of diethyl- and diphenyl-mercury, of phenylmercuric chloride and bromide, and of *n*-propylmercuric chloride has been studied in a flow system using low substrate pressures, in presence of a large excess of toluene, and short contact times. The mechanisms of the decompositions have been discussed and values for the activation energy and frequency factor have been obtained for each decomposition except that of *n*-propylmercuric chloride. It has been concluded that the data available for all the organomercury compounds which have been studied so far fall into two distinct classes with regard to activation energy and frequency factor. An attempt has been made to explain this division in terms of potential-energy surfaces.

Although previous work [Gowenlock, Polanyi, and Warhurst, (I) *Proc. Roy Soc.*, 1953, *A*, **218**, 269; Chilton and Gowenlock, *Trans. Faraday Soc.*, 1953, **49**, 1451; 1954, **50**, 824; Laurie and Long, *ibid.*, 1955, **51**, 665] on the thermal decomposition of mercury alkyls has not covered a wide field, the results obtained so far fall into two groups with regard to activation energy and frequency factor (see Table 2).

On the one hand is dimethylmercury, for which the activation energy of the homogeneous decomposition is undoubtedly less than the sum of the first and the second mercury–carbon bond-dissociation energies as determined by Mortimer, Pritchard, and Skinner (*ibid.*, 1952, **48**, 220) and by Carson, Carson, and Wilmshurst (*Nature*, 1952, **170**, 320) from thermochemical studies. There can be little doubt that in this case the activation energy can be accepted as a reliable figure for the dissociation energy, D_1, of the first mercury–carbon bond, *i.e.*, D(AlkHg–Alk). That, on this basis, the dissociation energy, D_2, of the second bond is much smaller than D_1, has been explained by Gowenlock, Polanyi, and Warhurst (II) (*Proc. Roy. Soc.*, 1953, *A*, **219**, 270). The frequency factor, ν, for the decomposition of dimethylmercury is about 3×10^{13}. Values of $\sim 10^{13}$ have been found for numerous bond-dissociation reactions by Szwarc and his collaborators (*Chem. Rev.*, 1950, **47**, 75) and are sometimes referred to as a " normal " frequency factor for a unimolecular reaction.

On the other hand, there are di-*n*- and di*iso*-propylmercury (Chilton and Gowenlock, *Trans. Faraday Soc.*, 1953, **49**, 1451; 1954, **50**, 824), for which the activation energies of the first-order decomposition are approximately equal to the *sum* of the first and the second dissociation energies (*i.e.*, to $D_1 + D_2$) and certainly larger than any plausible value of D_1. Also, for both reactions the frequency factor is in the range 10^{15}—10^{16}, at least 100 times larger than the so-called normal value. Chilton and Gowenlock, on the basis of a suggestion by Peard, Stubbs, and Hinshelwood (*Proc. Roy. Soc.*, 1952, *A*, **214**, 471) concerning the decomposition of certain hydrocarbons, consider that in the decomposition of these two mercury alkyls the activation energy is not localised in one bond but in both mercury–carbon bonds and the first step is assumed to be $Hg(Alk)_2 \longrightarrow Hg + 2Alk$, *i.e.*, the molecule breaks into *three* fragments.

The present work was initially a continuation of the work on dimethylmercury with a view to extending the determinations of mercury–carbon bond-dissociation energies. However, Chilton and Gowenlock's results for di-*n*- and di*iso*-propylmercury and our own observations on diphenylmercury showed that this aspect of pyrolytic work was limited. It appeared to us that, in addition to the amassing of further data on bond-dissociation energies, an extensive study of the pyrolysis of compounds of the types R_2Hg and RHgX, where R is an alkyl or aryl radical and X is a halogen atom, would be of interest in substantiating whether or not only two distinct types of behaviour are exhibited with regard to thermal decomposition. It was also considered that such an investigation might reveal connections between differences in behaviour and factors such as structural and energetic differences in the molecules.

EXPERIMENTAL

Preparation and Purification of Materials.—Diethylmercury, from Messrs. Light and Co. Ltd., was dried and fractionated under reduced pressure in an efficient column packed with stainless-steel gauze. The fraction collected between 46·0° and 46·3°/11 mm. was used in the pyrolysis experiments. Diphenylmercury (B.D.H.) was slowly sublimed in a good vacuum at a temperature just below its m. p. The middle sublimation fractions melted sharply at 124°. Phenylmercuric chloride and bromide and *n*-propylmercuric chloride were prepared by the same method, *viz.*, by mixing equimolar amounts of HgR_2 and HgX_2 in a suitable solvent. The precipitated RHgX was washed and recrystallised and then dried by thorough pumping *in vacuo.* The products melted sharply at 251°, 276°, and 145°, respectively. The di-*n*-propylmercury required for the preparation of *n*-propylmercuric chloride was prepared by Gilman and Brown's method (*J. Amer. Chem. Soc.*, 1930, **52**, 3314). The carrier gases, nitrogen and carbon dioxide (which was used in a few experiments only), were purified by slow passage through sodium vapour at 350°. The toluene was a special "sulphur low" product from Messrs. Hopkin and Williams Ltd. It was purified by " pre-pyrolysis " twice at 900°, followed by distillation in an efficient column.

Apparatus.—The apparatus used was that described by Gowenlock, Polanyi, and Warhurst (I) (*loc. cit.*). It consisted essentially of a circulation system through which nitrogen could be streamed at known pressures and known rates of flow. Immediately after leaving the circulation pump the nitrogen was completely freed from mercury (from the pump) by a U-tube system in which the gas was several times alternately heated to 200° and cooled to –195°. The flow was then split into two calibrated branches—a toluene branch, *T*, and a substrate branch, *S*. Toluene vapour was introduced into the carrier gas in *T*, and substrate vapour in *S*. The two streams then united and passed through the hot reaction vessel, after which the gases passed through a U-tube at 0° in which mercury, dibenzyl, and various other products, depending on the substrate investigated, were collected. The toluene was condensed out in a trap at –80° immediately after the U-tube, and a further trap at —195° ensured the removal of all volatile products with the exception of methane (if any) from the nitrogen stream. Before returning to the circulation pump, the nitrogen passed through a calibrated capillary across a double McLeod gauge for measurements of the rate of flow. Known vapour pressures (1—4 mm.) of toluene were maintained in the reaction vessel by saturating the nitrogen stream in branch *T* with the vapour from liquid toluene at a known temperature. A similar technique was used in branch *S* for substrate vapour pressures.

The method of analysis of the products which were condensed out in the U-tube varied with each compound investigated. For the experiments with diethylmercury in the presence of toluene, mercury, possibly with traces of dibenzyl, was the only condensate. The U-tube was rinsed with ether several times to remove dibenzyl, and the mercury determined by direct weighing. For experiments in which toluene was absent the rinsing process was omitted. In the pyrolysis experiments with compounds PhHgX (X = Cl or Br), which were all carried out in the presence of toluene, the possible products in the U-tube are mercury, dibenzyl, diphenyl, mercurous halide, and unchanged PhHgX. The U-tube was washed several times with boiling toluene, rinsed with ether, dried, and weighed. This extraction removes dibenzyl, diphenyl, and PhHgX. The residue was then treated with hot potassium iodide solution, and the U-tube rinsed with water, acetone, and ether, dried, and re-weighed. This treatment converts mercurous halide into a soluble complex and liberates half the mercury as free metal. The total free mercury which remained in the U-tube was determined by direct weighing. These weighing give the separate amounts of mercury and Hg_2X_2. In experiments with Ph·HgCl the above procedure showed that, in the conditions used, the amounts of mercurous chloride were a very small fraction of the total mercury in the products. Consequently, for increased speed of working, the treatment with potassium iodide could be omitted without incurring significant errors in the velocity-constant determinations. For *n*-propylmercuric chloride the full analytical method described above was applied, except that acetone was used instead of toluene for the preliminary extraction. The reliability of the various extraction processes was checked by blank experiments.

Volatile products, such as certain hydrocarbons and hydrogen chloride and bromide, were estimated by pumping the gases from the main apparatus into an analytical section in which the pressures exerted by each gas in a calibrated volume space could be measured. In many cases the process of transferring the various volatile fractions to the analytical section involved careful selective refrigeration of the trap in the main apparatus from which the products were being distilled. The degree of unsaturation of hydrocarbon fractions was determined in the analytical section by Robb and Melville's technique (*Proc. Roy. Soc.*, 1949, *A*, **196**, 445), and in a few experiments also by absorption of the unsaturated hydrocarbons in concentrated sulphuric acid containing silver sulphate (Gooderham, *J. Soc. Chem. Ind.*, 1938, **57**, 388) : the two methods gave results in reasonable agreement.

Two methods were used for the determination of the amounts of hydrogen halides produced. In some experiments the gas was pumped from the main apparatus to the analytical section, and its pressure measured. For fractions in which the hydrogen halide could not be easily separated from hydrocarbons, the drop in pressure on absorption of the halide by saturated aqueous potassium hydroxide was measured. The other method consisted in distilling the hydrogen halide into a side trap in the main apparatus in which the contents could then be dissolved in water and the acid determined by the liberation of iodine from iodide–iodate solution. We are not satisfied with either of these methods. Compared with our mercury and hydrocarbon determinations, the results were not very reproducible and we have only used them in a qualitative way in our Discussion.

Most of the pyrolyses were carried out within the following range of experimental conditions : total pressure in reaction vessel = 10 ± 1 mm.; time of contact = 0·1—0·3 sec.; decomposition = 10—75%; substrate pressure in reaction vessel = 1—10 × 10^{-2} mm.; and (toluene/substrate) ratios in the reaction vessel of 30—200. A typical set of results at one temperature

TABLE 1.

Compound	Temp.	$100P_{\text{substrate}}$ (mm.)	$\frac{P_{\text{toluene}}}{P_{\text{substrate}}}$	τ (sec.)	Decompn. (%) † I	II	Vel. const., k (sec.$^{-1}$)
Ph·HgCl	703°	4·15	47	0·190	12·2	—	0·683
	703	4·48	43	0·202	16·0	—	0·859
	703	4·08	47	0·244	17·1	—	0·766
$HgPh_2$	658	1·31	140	0·161	20·0	—	1·39
	658	1·41	136	0·145	18·3	—	1·40
	658	2·51	77	0·401	38·6	—	1·22
	658	3·53	54	0·444	42·1	—	1·23
	658	1·11	173	0·142	15·5	—	1·19
$HgEt_2$	370	12·0	*	0·351	19·9	26·8	0·633
	370	12·0	*	0·317	17·7	17·7	0·616
	370	12·0	*	0·365	20·4	20·1	0·621
	370	9·0	34	0·303	15·6	15·2	0·552
	370	9·0	34	0·296	18·2	16·6	0·646
	370	9·0	32	0·225	12·5	13·2	0·613
Ph·HgBr	701	6·29	46	0·267	41·8	—	2·00
	702	3·34	81	0·168	28·3	—	1·98
	702	5·33	51	0·275	39·7	—	1·84
Pr^n·HgCl	564	4·82	89	0·142	10·6	18·3	0·79
	564	5·50	79	0·140	11·7	17·2	0·89
	565	8·27	52	0·182	24·6	17·4	1·55
	563	13·8	31	0·126	27·2	26·5	2·53

* Toluene absent.

† The figures for the percentage decomposition for Ph·HgCl, $HgPh_2$, and $HgEt_2$ given in the column labelled I are based on the yield of mercury; those for Ph·HgBr and Pr^n·HgCl are based on the yield of $(Hg + 2Hg_2X_2)$. The figures for the percentage decomposition given in the column labelled II are based on the yield of $(C_4 + \frac{1}{2}C_2)$ for $HgEt_2$ and on $(\frac{1}{3}C_1 + \frac{2}{3}C_2 + C_3)$ for Pr^nHgCl.

for each compound is shown in Table 1. The velocity constants have been calculated from $k = (1/\tau) \ln 100/(100-f)$, where τ is the time of contact in seconds, and is equal to

$$\frac{\text{Effective volume of reaction vessel}}{\text{Volume flow through reaction vessel}}$$

and f = the percentage decomposition $= 100P/S$, where S and P are the number of moles of substrate and relevant product which pass through the reaction vessel during the time of the experiment. For diethylmercury values of f were calculated both from the weight of mercury and from the yield of $C_4H_{10} + \frac{1}{2}(C_2H_6 + C_2H_4)$, which were the only hydrocarbon products. Velocity constants were calculated from the mean of the two values for f. For diphenylmercury and phenylmercuric chloride the values of f were calculated from the mercury yield. As mentioned above, the fact that, in the latter case, a very small fraction of the weighed product was mercurous chloride could be ignored. The f values for phenylmercuric bromide and propylmercuric chloride were based on the yields of $Hg + 2Hg_2X_2$. In connection with the values of f for the last two compounds and phenylmercuric chloride, it should be emphasised that, because of the large atomic weight of mercury, the values of k are very insensitive to relatively large errors in the determination of the *proportions* of mercury and mercurous halide in the products.

For all the compounds investigated, except *n*-propylmercuric chloride, the kinetics were of the first order in substrate concentration. Changes in substrate concentration and in the time of contact over a range of 2—4-fold produced no significant drift in the values of k (for some examples, see Table 1). Figs. 1 and 2 show the results as Arrhenius plots of log k against $1/T$. Two sets of results are shown for diphenylmercury. The dotted circles and dotted line correspond to some early experiments. By comparing the results of substrate vapour-pressure calibrations at the end of this series with those at the beginning, it was found that the degree of saturation of the carrier gas stream in the S branch had decreased considerably. The sequence of runs started at the lowest temperature and worked progressively up to the highest. As a consequence, although the data cannot provide an accurate value for the activation energy, they give, unambiguously, a lower limit of ~ 63 kcal. for this quantity. The full circles and straight line correspond to experiments in which the above defect was eliminated and we attach more importance to these results.

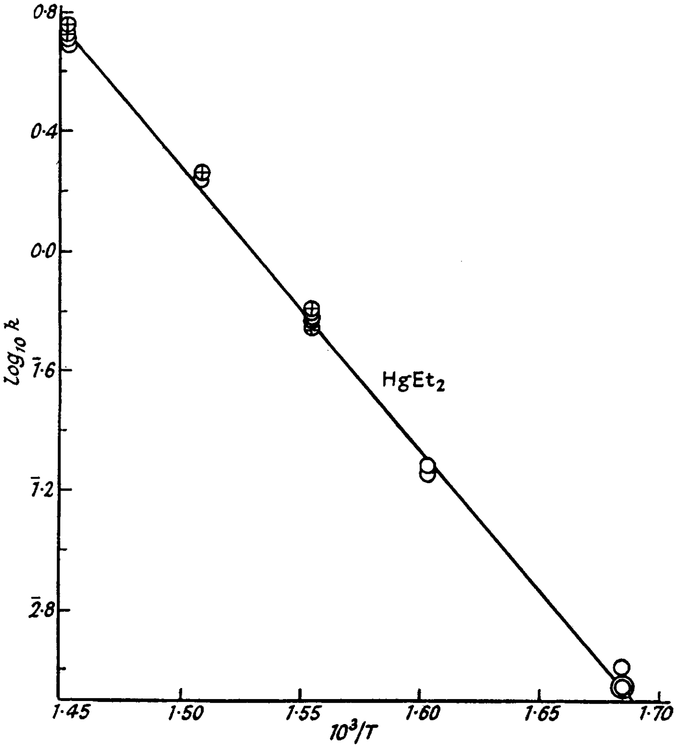
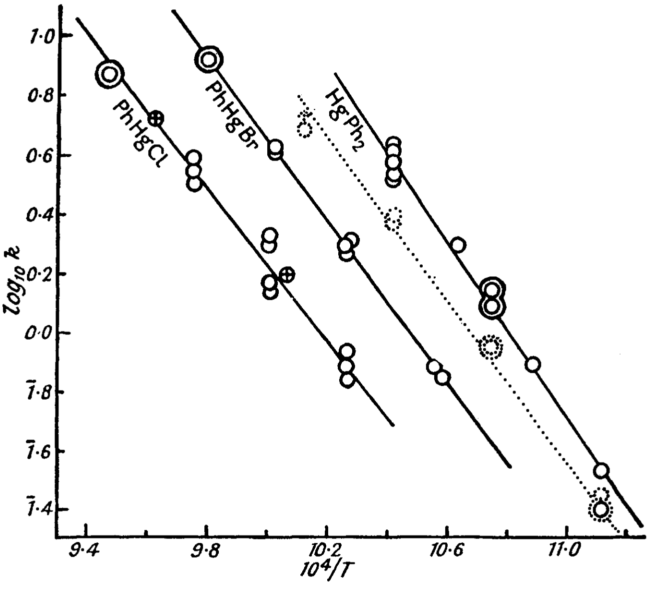


FIG. 1.

○, *Toluene absent.*
⊕, *Toluene/substrate ratio,* ~30.

FIG. 2. *Toluene present in all experiments.*

⊕ *includes the small amount of* Hg_2Cl_2 *in the product.*



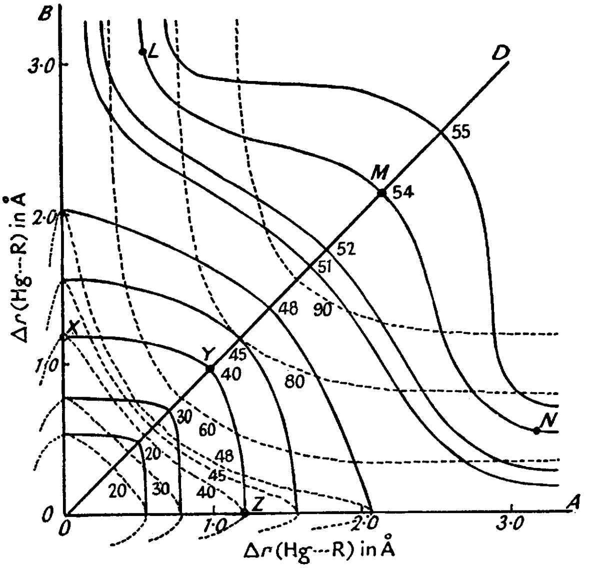


FIG. 3.

(*Contours in kcal. mole*$^{-1}$.)

DISCUSSION

Reaction Mechanisms.—The apparatus was not designed for detailed determinations of all the products in each of the thermal decompositions studied. This is not necessary for the determination of velocity constants. Nevertheless, plausible mechanisms can be suggested in most cases, and supported, in some instances, by a certain amount of experimental evidence.

Diethylmercury.—The general features of this pyrolysis in the absence of toluene were as follows. The only hydrocarbons produced in any appreciable quantities were ethane, ethylene, and butane. The ratios ethane/ethylene (≈ 1) and C_4/C_2 (≈ 4) were both practically independent of temperature. These rough observations are in agreement with the more detailed and accurate work of Ivin and Steacie (*Proc. Roy. Soc.*, 1951, *A*, **208**, 25) on the photolysis of diethylmercury. There can be little doubt that the principal reactions involved are :

$$(C_2H_5)_2Hg \xrightarrow{k_1} C_2H_5Hg + C_2H_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$C_2H_5Hg \xrightarrow{k_2} C_2H_5 + Hg \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$C_2H_5 + C_2H_5 \xrightarrow{k_3} C_4H_{10} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$C_2H_5 + C_2H_5 \xrightarrow{k_4} C_2H_4 + C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Of these reactions, (3) and (4) have nearly the same activation energy (Ivin and Steacie find $E_4 - E_3 \sim 0{\cdot}8$ kcal. mole^{-1}). For reasons given below we believe this molecule to belong to the same class as dimethylmercury, the first step in the thermal decomposition being a dissociation into two fragments. Application of the stationary-state method to the above mechanism gives :

$$d[C_4 + \tfrac{1}{2}C_2]/dt = d[Hg]/dt = k_2[C_2H_5Hg] = k_1[Hg(C_2H_5)_2]$$

It can be seen from the Arrhenius plot shown in Fig. 1 that the presence of toluene, at concentrations more than 30 times that of the substrate, has no effect on the velocity constant. It was also found to have only a very minor effect on the hydrocarbon composition. This indicates that the reaction between ethyl radicals and toluene at about 350° is slower than reactions (3) and (4). Similar observations with regard to methyl radicals and toluene at about 250° have been reported by Murawski, Roberts, and Szwarc (*J. Chem. Physics*, 1951, **19**, 698).

Phenylmercury Halides.—We can discuss the pyrolysis of phenylmercuric chloride and bromide together, using X to represent the halogen atom. There are three general aspects of interest with regard to the mechanism. They are : (*a*) the ratio Hg/Hg_2X_2 increases with increasing temperature, (*b*) at the same temperature $Hg/Hg_2Cl_2 > Hg/HgBr_2$, and (*c*) although our analytical results for HX are not very satisfactory, there is no doubt that the ratio $Hg/HX > 1$. These observations can be accounted for by the following mechanism :

$$\mathrm{PhHgX} \xrightarrow{k_5} \mathrm{Ph\cdot} + \mathrm{HgX\cdot} \quad . \quad . \quad . \quad . \quad (5)$$

$$\mathrm{Ph\cdot} + \mathrm{CH_3Ph} \xrightarrow{k_6} \mathrm{PhH} + \mathrm{\cdot CH_2Ph} \quad . \quad . \quad . \quad . \quad (6)$$

$$\mathrm{Ph\cdot} + \mathrm{Ph\cdot} \xrightarrow{k_7} \mathrm{Ph_2} \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathrm{HgX} + \mathrm{CH_3Ph} \xrightarrow{k_8} \mathrm{Hg} + \mathrm{XH} + \mathrm{\cdot CH_2Ph} \quad . \quad . \quad . \quad . \quad (8)$$

$$\mathrm{HgX} + \mathrm{HgX} \xrightarrow{k_9} \mathrm{Hg} + \mathrm{HgX_2} \xrightarrow[\text{exit tube}]{\text{In the cold}} \mathrm{Hg_2X_2} \quad . \quad . \quad . \quad . \quad (9)$$

$$\mathrm{HgX} + \mathrm{Ph\cdot} \xrightarrow{k_{10}} \mathrm{Hg} + \mathrm{PhX} \quad . \quad . \quad . \quad . \quad (10)$$

There are a number of possibilities for the fate of the HgX radical. We have rejected the dissociation of HgX, by either a unimolecular or a bimolecular (*i.e.*, by collision with toluene or nitrogen molecules) process since, in order to account for the appearance of Hg_2X_2 in the products, it would be necessary to postulate that some X atoms escaping reaction emerged from the reaction vessel. This is exceedingly unlikely in view of the relatively large pressure of toluene with which it is known that both chlorine and bromine atoms react extremely rapidly (see, *e.g.*, Anderson, Scheraga, and Van Artsdalen, *J. Chem. Physics*, 1953, **21**, 1258; Szwarc and Williams, *Proc. Roy. Soc.*, 1953, *A*, **219**, 353; Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629; Szwarc and Taylor, *J. Chem. Phys.*, 1954, **22**, 270). We have chosen reaction (9) to account for the presence of Hg_2X_2 in the products since, for both X = Cl and Br, the reaction is more than 50 kcal. mole^{-1} exothermic and would be expected to be very fast with a negligible activation energy. Reaction (8) is regarded as the main mercury-producing reaction and is about 1 kcal. exothermic and 7 kcal. endothermic for X = Cl and Br, respectively. It is not unreasonable to expect, therefore, activation energies of 5—10 kcal. mole^{-1} for the chloride and 10—15 for the bromide. These values, together with the high concentration of toluene, would explain why reaction (8) is able to compete effectively with reaction (9). The assumption that $E_8 > E_9$ accounts for the increase in the Hg/Hg_2X_2 ratio with increase in temperature. The assumption that E_8 (X = Br) $> E_8$ (X = Cl) while $E_9 \approx 0$, for both X = Cl and Br, would account for the fact that $Hg/Hg_2Br_2 < Hg/Hg_2Cl_2$ for a given temperature. Reaction (10) accounts for the fact that the ratio Hg/HX is greater than unity. Application of the stationary state method to the mechanism gives :

$$d[\mathrm{Hg} + 2\mathrm{Hg_2X_2}]/dt = k_8[\mathrm{HgX}][\mathrm{PhCH_3}] + k_{10}[\mathrm{Ph}][\mathrm{HgX}] + 2k_9[\mathrm{HgX}]^2 = k_5[\mathrm{PhHgX}]$$

Diphenylmercury. We did not attempt to determine the hydrocarbon products of the pyrolysis of this compound. It is extremely probable that the mechanism is :

$$\mathrm{HgPh_2} \xrightarrow{k_{11}} \mathrm{Hg} + 2\mathrm{Ph\cdot} \quad . \quad . \quad . \quad . \quad (11)$$

$$\mathrm{Ph\cdot} + \mathrm{Ph\cdot} \xrightarrow{k_{12}} \mathrm{Ph_2} \quad . \quad . \quad . \quad . \quad (12)$$

$$\mathrm{Ph\cdot} + \mathrm{CH_3Ph} \xrightarrow{k_{13}} \mathrm{PhH} + \mathrm{\cdot CH_2Ph} \quad . \quad . \quad . \quad . \quad (13)$$

For reasons given later, we consider that the first step in the decomposition breaks both Hg–C bonds and gives three fragments.

n-*Propylmercuric chloride.* Decomposition of this was much more complex than that of the other molecules studied; it was not of first order in substrate concentration (see Table 1) and the mechanism involves chain reactions. The nature of the hydrocarbon products showed that nearly all the propyl radicals produced decomposed into methyl radicals and ethylene. The chain reaction (or reactions) probably involves attack of the substrate by methyl radicals. It was not possible to derive a value for activation energy from our results. We think that this complexity will very probably apply to all molecules of the type AlkHgX, with the possible exceptions of CH_3HgX. The Alk–HgX dissociation energy values given by Mortimer, Pritchard, and Skinner (*Trans. Faraday Soc.*, 1952, **48**, 220) and Hartley, Pritchard, and Skinner (*ibid.*, 1951, **47**, 254) indicate that the pyrolysis of these compounds would necessitate relatively high temperatures, in the range 650—750°. Our experience with *n*-propylmercuric chloride suggests that at such temperatures the kinetics would not be straightforward.

Activation Energies and Frequency Factors.—The value of E * and ν for the decompositions which we have studied, together with earlier examples and the relevant thermochemical data, are collected in Table 2.

TABLE 2. (All energies in kcal. mole^{-1}.)

Molecule	$D_1 + D_2$	D_1	D_2	E	log ν
$HgMe_2$	$57{\cdot}3 \pm 4$ [a]	$51{\cdot}5 \pm 2$	~6	$51{\cdot}5 \pm 2$ [c]	13·5 [c]
	$57{\cdot}1 \pm 2$ [b]			$51{\cdot}3 \pm 0{\cdot}5$ [d]	14·3 [d]
$HgEt_2$	$45{\cdot}1 \pm 6$ [a]	$42{\cdot}5 \pm 2$	~5	$42{\cdot}5 \pm 2$	14·1
	48·5 [a]				
PhHgCl	$(81{\cdot}6 \pm 3)$ [e]	$(58{\cdot}6 \pm 3)$	23	59 ± 3	13·0
	$85{\cdot}8 \pm 3$ [e]	$62{\cdot}8 \pm 3$ [e]			
PhHgBr	$(75{\cdot}7 \pm 3)$ [e]	$(58{\cdot}7 \pm 3)$ [e]	17	63 ± 2	14·3
	$79{\cdot}9 \pm 3$ [e]	$62{\cdot}9 \pm 3$ [e]			
$HgPh_2$	$(55{\cdot}4 \pm 9)$ [f]	—	—	68 ± 4	16·0
	$63{\cdot}8 \pm 9$			>63	
$HgPr^n_2$	$49{\cdot}4 \pm 4$ [a]	—	—	46·5 [g]	15·3 [g]
$HgPr^i_2$	$40{\cdot}3 \pm 7$ [a]	—	—	$40{\cdot}4 \pm 1$ [h]	16·7 [h]

[a] Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220. [b] Carson, Carson, and Wilmhurst, *Nature*, 1952, **170**, 320. [c] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269. [d] Laurie and Long, *Trans. Faraday Soc.*, 1955, **51**, 665. [e] Pritchard, Thesis, Manchester, 1951. [f] Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1951, **47**, 254. [g] Chilton and Gowenlock, *ibid.*, 1954, **50**, 824. [h] *Idem, ibid.*, 1953, **49**, 1451.

The figures given in parentheses for Ph·HgCl, Ph·HgBr, and $HgPh_2$ are based on D(Ph–H) = 97·8 kcal. [see ref. (*e*)]; the corresponding figures without parentheses are based on D(Ph–H) = 102 kcal.

The results for phenylmercuric chloride and bromide show that the pyrolytic method can yield good values for D_1. The agreement between our values of E and Pritchard's values of D_1 (Thesis, Manchester, 1951) from thermochemical measurements is as good as can be expected. It was merely a very reasonable inference by Gowenlock, Polanyi, and Warhurst (I) (*loc. cit.*) that their value of 51·5 for the activation energy of decomposition of dimethylmercury was a good value for D_1. The results for phenylmercuric chloride and bromide strengthen this inference considerably. Our results for diethylmercury now firmly establish the activation energy for this decomposition as $42{\cdot}5 \pm 2$ kcal. mole^{-1}, and since this is appreciably lower than the probable thermochemical value for $D_1 + D_2$, we believe that it is a good value for D_1. The earlier figure of 41·5 given by Gowenlock, Polanyi, and Warhurst (I) (*loc. cit.*) was based on the assumption that the frequency factors for the decompositions of dimethyl- and diethyl-mercury were identical.

We consider that the data given in Table 2 for the seven organomercury compounds studied so far substantiate the suggestion that each compound belongs to one or other of two distinct classes with regard to its behaviour on thermal decomposition. Class I, which consists of $HgMe_2$, $HgEt_2$, PhHgCl, and PhHgBr, is characterised by $D_1 + D_2 > E = D_1$

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* The values given in the Table for the compounds we have investigated have been derived as follows. The method of least squares has been applied to each set of data and the value of E obtained from the resulting slope has been decreased by 0·5 kcal. to allow for the fact that the velocity constants at the lower end of the temperature range are less accurate than at the higher end, the likely errors being such as to make the low-temperature constants too small.

and log $\nu = 13{\cdot}7 \pm 0{\cdot}7$, *i.e.*, frequency factors in the so-called " normal " range. Class II consists of $HgPr^n_2$, $HgPr^i_2$, and $HgPh_2$ and is characterised by $E \approx D_1 + D_2$ and log $\nu = 16 \pm 0{\cdot}7$. This important feature merits further discussion. Consider class II : if these decompositions actually involved the breaking of only one bond, then it would be necessary to assume that phenyl, *iso*propyl, and *n*-propyl groups, for some reason, caused the potential-energy curve for the bond dissociation to possess a hump, the height of which happened to be equal to the particular value of D_2 in each case. This seems extremely unlikely and we adopt the view that this class of compound decomposes into three fragments in one step, the activation energy being identified with $D_1 + D_2$. We also consider it very unlikely that this characteristic of class II arises because the values of D_2 are zero. Of all the examples of HgR radicals, it would be expected that HgPh would possess the strongest bond because of the possibility of conjugation involving orbitals of the mercury atom and the π electrons of the benzene ring. Turning to class I, it seems evident that the main reason why the first step in the dissociation of phenylmercuric chloride and bromide involves the rupture of one bond only is because D_2 for these two cases is relatively large. Increases in activation energy of 23 and 17 kcal. mole^{-1}, respectively, are probably too large to be offset by increases in frequency factor. However, the size of D_2 cannot be the sole cause for the division into two classes, since dimethylmercury, which dissociates into two fragments, almost certainly has a value of D_2 which is smaller than that for diphenylmercury.

Dissociation of the molecule HgR_2 into three fragments clearly causes a change from the bivalent to the zero-valent state in the mercury atom. Gowenlock, Polanyi, and Warhurst (II) (*loc. cit.*) have shown that this also occurs when the molecule dissociates into two fragments, Hg^0R and R, and that this is responsible for the striking feature in the thermochemistry of the mercury alkyls, *viz.*, that $D_1 + D_2$ is only a little larger than D_1. It is of some interest to examine the detailed energetics of the two possible modes of decomposition. Fig. 3 shows two potential-energy surfaces for configurations of the HgR_2 molecule. The first, drawn in broken curves, depicts the situation when the two Hg–R bonds in the molecule are *completely independent of each other.* The relevant potential-energy curve applicable to extensions of either of the two bonds was assumed to be the Morse function $V = 50[1 - \exp(-1{\cdot}87\Delta r)]^2$, where V is the potential energy relative to the unstretched state as zero, Δr is the bond extension, and the Morse constant $a = 1{\cdot}87$ has been derived from the value of the force constant ($2{\cdot}4 \times 10^5$ dynes cm.$^{-1}$) calculated by Thompson and Linnett (*Proc. Roy. Soc.*, 1937, *A*, **160**, 593) for the bonds in dimethylmercury. A typical value of 50 kcal. has been chosen for the energy of dissociation of either of the two bonds. This first energy surface is obtained when it is assumed that the above Morse curve applies to extensions of one of the mercury–carbon bonds *irrespective of the state of extension of the other.* This means that the dissociation energy of the HgR radical is also 50 kcal. This surface, which is very similar to that constructed by Goodeve (*Trans. Faraday Soc.*, 1934, **30**, 60) for the carbon dioxide molecule, consists of two valleys (each parallel to a co-ordinate axis) and a high plateau. Dissociation into two fragments corresponds to moving up one or other of the valleys from *O* (the ground state of the molecule) to *A* or *B*, with an increase in potential energy of $D_1 = 50$ kcal. Dissociation into three fragments corresponds to moving from *O* to *D* on the plateau, with an increase of potential energy of $2D_1$, *i.e.*, 100 kcal., the path along the diagonal being much steeper than that along the valleys. In these circumstances the molecule HgR_2 would clearly dissociate into two fragments with $E = D_1$. Further, the molecule being considered as a three-particle system, it is clear that only the unsymmetrical mode of vibration ν_3 will be relevant. On these grounds a frequency factor of $\sim 10^{13}$ might be expected.

The second potential-energy surface, drawn in full curves, represents an attempt to describe approximately the state of affairs for a " real " mercury alkyl, which differs from the above case in two important aspects, *viz.*, (*a*) that $D_1 + D_2 = D_1 + 6$, which gives a very low plateau, and (*b*) that the two bonds are not energetically independent. For example, in the simultaneous, symmetrical stretching of the molecule the dissociation limit for *each* bond must now be $(D_1 + D_2)/2$, *i.e.*, 28 kcal. and not 50 kcal., as for the first surface. The full details of this bond interdependence are extremely difficult, if not at present impossible, to assess. We have attempted to deal with it for symmetrical stretched configurations only, *i.e.*, for points on the diagonal of the potential-energy surface. For these we have assumed that the Morse constant of 1·87 still applies, *i.e.*, that the energy of a point on the diagonal is given by $V = 2 \times 28[1 - \exp(-1{\cdot}87\Delta r)]^2$. The energy changes for stretching one bond only, *i.e.*, moving from *O* to *A* or *B*, are again given by the expression $V = 50(1 - \exp -1{\cdot}87\Delta r)^2$. For total energies in the region $56 > V > 50$, we need the potential curve for the dissociation of the "real" HgR radical. We have used the Morse function $V = 6[1 - \exp(-a\Delta r)]^2$ for this, the constant *a* being derived from the force constant of the very similar molecule, HgH. The exact shape of this curve is of minor importance in our discussion. Our method of plotting the second energy surface, using the above three Morse functions, thus gives us only three points per energy contour, *e.g.*, *X*, *Y*, *Z* for $50 > V > 0$ and *L*, *M*, *N* for $56 > V > 50$, and, to obtain merely the general features of the surface, we have sketched the contours very roughly from these points, utilising, of course, a number of obvious trends which the contours must follow, for example, as they approach very large values for one of the bond lengths.

The second surface shows a striking contrast to the first in that the two distinct valleys have vanished, leaving a broad shallow basin, symmetrical about the diagonal.* We believe that this aspect is probably real and does not arise from the crudity of our methods. The important configurations are actually those on the diagonal, and it does not appear likely that the uncertainties in the assumed potential function for these configurations could be solely responsible for the disappearance of the two valleys. This basin-like form of the second surface has the consequence that the difference in steepness between the diagonal path *OD* and the paths *OA* and *OB* is much less than that for the first surface, *i.e.*, dissociation into three fragments becomes relatively much more likely. Further, for configurations represented by points in the basin near the diagonal, it is clear that more than one fundamental mode of vibration is important for the dissociation into three fragments; the symmetrical modes ν_1 and the doubly degenerate ν_2 are all relevant. On these grounds it is reasonable to expect an increased frequency factor for this type of decomposition. We suggest tentatively that the precise details of the membership of the various organomercury compounds in the two classes of behaviour may depend very sensitively on the curvature of the basin-like surface in the region of the diagonal, and that for members of class II the basin-like character may have become so pronounced that the diagonal path is actually less steep than the *OA* or *OB* paths, whereas for class I this is not so. One of the important factors which affects the curvature of the surface in this region is the following. In the unstretched state, the molecule can be represented by the valency-bond configuration R–Hg^{II}–R, with very little contribution from the structure R–Hg^0–R, in which the mercury atom is zero-valent. When the molecule is stretched the contribution of the latter structure increases at the expense of the former. This is the most important factor which is responsible for the interdependence of the two bonds in the molecule. With two different organomercury compounds, there may be appreciable differences in the rate at which the contribution of the zero-valent structure increases when the bonds are stretched and this would produce differences in the curvature of the energy surfaces.

We thank the D.S.I.R. for a grant (to E .I. C.).

THE UNIVERSITY, MANCHESTER, 13. [*Received, July 8th*, 1955.]

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* We have rejected the possibility that the surface consists of *three* valleys (one along each of the co-ordinate axes and one along the diagonal) for the following reason. If one of the bonds were stretched to an extent corresponding to the point *X*, say, in Fig. 3, then on stretching the other bond, corresponding to moving from *X* in a direction parallel to *OA*, it is found that this extension curve would possess at least *two* points of inflexion. We consider that this is extremely unlikely; a normal bond extension curve only possesses *one* point of inflexion.