

tion of the mass spectra of decaborane in which the bridge positions were deuterated.²¹ The monoisotopic spectra indicate the loss of H in pairs, and they found in the deuterated case that a high percentage of these pairs consisted of one terminal proton and one bridge deuterium. Nearly all the transitions postulated here involve a bridge and terminal proton. Finally the structure for $B_4H_6^+$ is the same as that postulated from appearance potential measurements of the fragments from $B^{11}_5H_9$.⁸

From the appearance potential data, it can be seen that the activation energies for the transition states involved in the decomposition reactions are approximately 2 e.v. or less. This is comparable to those determined for butane.²²

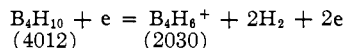
In the usual manner,^{8,23} one can also calculate the ionization potentials of the fragment ions from their appearance potentials, if it is assumed the structure of the product is given by the above diagram and 2H leaves as H_2 molecules when possible. For example,

(21) I. Shapiro, M. Lusty and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 838 (1959).

(22) H. M. Rosenstock and C. E. Melton, *J. Chem. Phys.*, **26**, 314 (1957).

(23) W. J. Dunning, *Quart. Rev.*, **9**, 23 (1955).

consider $B_4H_6^+$. One can write the strictly formal process for the formation of this ion from B_4H_{10} as



$$I(B_4H_6) = A(B_4H_6^+) + 2D(H_2) - 2D(B-H) - 2D(B-H-B) + 2D(B-B)$$

taking²⁴

$$\begin{aligned} D(H_2) &= 4.5 \\ D(B-H) &= 4.0 \\ D(B-H-B) &= 4.7 \\ D(B-B) &= 3.6 \end{aligned}$$

one obtains

$$I(B_4H_6) = 11.2 + 9.0 - 8.0 - 9.4 + 7.2 = 10.0 \pm 0.1$$

which agrees rather well with $I(B_4H_6) = 10.2 \pm 0.2$ obtained from the appearance potential of $B_4H_6^+$ from B_5H_9 .⁸ The calculated ionization potentials for the protonated compound are given in Table IV.

Acknowledgment.—The mass spectrometer used in this study was obtained in part through a grant from the National Science Foundation. T. F. is indebted to the Kennecott Copper Corporation for its support through a graduate fellowship for two years.

(24) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

The Reactions of Iodine in Solution with Elementary Mercury

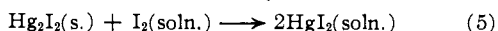
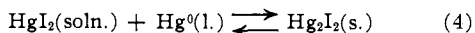
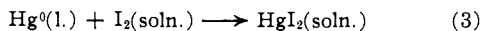
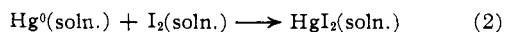
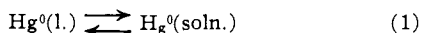
By PERCY WARRICK, JR., EUGENE M. WEWERKA AND MAURICE M. KREEVOY¹

RECEIVED SEPTEMBER 7, 1962

Iodine in a stirred solution in isoöctane in contact with a sizable, unbroken, droplet of mercury reacts *via* a number of paths. (1) The mercury dissolves in the isoöctane and once in solution reacts with the iodine at a rapid rate, producing mercuric iodide. (2) Iodine reacts with the metallic surface, producing mercuric iodide; the rate of this process can be controlled either by transport or chemical considerations, depending on the stirring rate. (3) Mercuric iodide, produced in processes 1 and 2, reacts with the metallic surface giving (solid) mercurous iodide. As long as excess iodine remains each mole of mercurous iodide is rapidly converted to two moles of mercuric iodide, but after the iodine is entirely consumed mercurous iodide accumulates as the ultimate product. Suitable rate laws are derived and observed rates are shown to obey them. Process 2 has a small, negative ΔH^\ddagger and a large negative apparent ΔS^\ddagger under conditions where it is not transport limited. This is rationalized on the basis of a one-electron transfer rate-determining step.

A large number of important reactions seem to proceed at metal-solution interfaces, but for the most part the detailed mechanism of these reactions is not known. Reactions taking place at the surface of metallic mercury seem to be particularly amenable to mechanistic study because the surface area is reproducible and roughly calculable. The present report primarily concerns the reaction of iodine in solution with metallic mercury. "Isoöctane" (2,2,4-trimethylpentane) was the solvent used for most of this work, but some work was also done in water as a solvent. The problems attacked are: (1) the identification of the actual reacting species and the first products of each reaction; (2) distinguishing between transport-controlled and chemically-controlled reactions; (3) deduction of mechanism for chemically-controlled reactions.

The following reactions were found to be significant



The rates of all these processes have been examined, but attention is focused on the reaction shown in eq. 3.

The rate constants for reactions taking place at the surface of the liquid mercury sample are indicated as

(1) Alfred P. Sloan Foundation Fellow, 1960-1964.

k_n^x where x is the substance being consumed from solution and n is the apparent order with respect to that substance. In most cases a 17.6-g. mercury sample with an exposed area of 11.2 cm.² was used. Exceptions are individually noted.

Results

In all of the work with metallic mercury described below, the mercury was an unbroken drop of known mass remaining relatively stationary at the bottom of a round-bottom flask. The solution above it was stirred mechanically. Samples were withdrawn periodically, analyzed spectrophotometrically, and then returned to the flask.

Mercury in Solution.—In order to evaluate the role played by the homogeneous solution reaction, eq. 2, in the presence of liquid mercury, the rate of the reaction between mercury atoms and iodine molecules in homogeneous solution in isoöctane was estimated by following the disappearance of the characteristic mercury peak at 257 $m\mu$. Both reagents were initially present at about $5 \times 10^{-6} M$ concentration. The rate was too fast to measure. If the reaction was first order with respect to each reagent it had a rate constant, k_2 , $> 10^4$ l. mole⁻¹ sec.⁻¹ at 25°. The product was shown to be mercuric iodide by its ultraviolet spectrum.

A plausible rate law for the solution of elementary mercury from a drop of fixed size is shown in eq. 6 in which k_0 is the rate of solution and the second term is the rate of precipitation.

$$d(\text{Hg}^0)/dt = k_0 - k_1^{\text{Hg}}(\text{Hg}^0) \quad (6)$$

Noting that the rate of solution and precipitation must be equal at equilibrium, eq. 6 can be integrated to give eq. 7 which is a standard first-order rate law. The re-

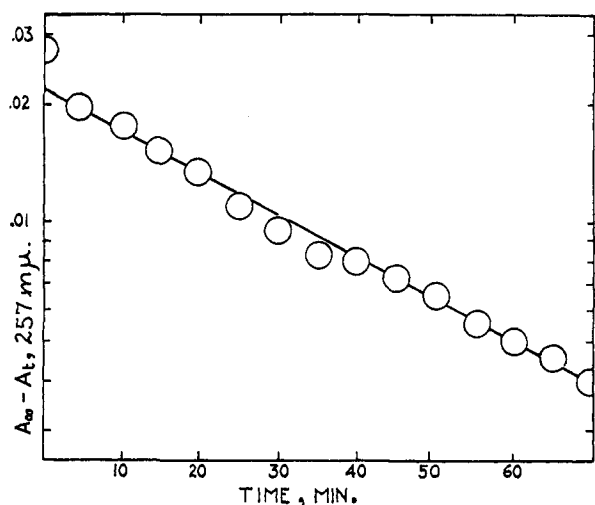


Fig. 1.—A plot of $\log(A_\infty - A_t)$ at $257 \text{ m}\mu$ vs. time at 25° and 400 r.p.m. From the slope of this plot k_1^{Hg} can be evaluated.

sults of a typical test of this rate law are shown in Fig. 1. Similar plots were made for temperatures ranging from

$$\ln \left\{ \frac{(\text{Hg}^0)_e - (\text{Hg}^0)_t}{(\text{Hg}^0)_e - (\text{Hg}^0)_i} \right\} = k_1^{\text{Hg}}(t - t_0) \quad (7)$$

0 to 70° and values of k_1^{Hg} were obtained from them by visual estimation. They are listed in Table I.

TABLE I

RATES OF SOLUTION AND REPRECIPITATION OF ELEMENTARY MERCURY AT STIRRING RATE 600 R.P.M.

$T, ^\circ\text{C.}$	$10^2 k_1^{\text{Hg}}, \text{ sec.}^{-1}$	$10^2 k_0, \text{ g. atom/l. sec.}$	$10^6 (\text{Hg}^0)_e, \text{ g. atom/l.}$
0	0.6	0.1	1.8
25	1.4	0.7	4.6
40	1.3	1.3	9.9
55	1.7	3.4	20
70	1.1 ^a	5.6 ^a	52

^a These values are less reliable than the others because the optical density of a saturated solution fell with time at this temperature.

The solubility of mercury in isoöctane at 25° is $4.6 \times 10^{-6} M$.² From this and A_∞ , the optical density of a saturated solution, ϵ_{257} (the Beer's law constant for mercury in isoöctane at $257 \text{ m}\mu$) can be obtained. From ϵ_{257} and A_∞ , solubilities and k_0 values were obtained at other temperatures. These are listed in Table I. The temperature dependence of $(\text{Hg}^0)_e$ is in fair agreement with that reported by Klehr³ and leads to a value of 9.0 kcal. mole⁻¹ for ΔH^0 of solution. Klehr's results in *n*-decane and toluene were 8.00 and 9.55 kcal. mole⁻¹, respectively. It is noteworthy that most of the temperature dependence of $(\text{Hg}^0)_e$ seems to come from the temperature dependence of the solution rate so that ΔH^\ddagger for the solution reaction is roughly equal to ΔH^0 . The reprecipitation rate constants do not seem to be accurate enough to justify the calculation of ΔH^\ddagger for this process. It seems to be small but positive. It seems likely that rates per unit surface area can be obtained by dividing any of the foregoing rate constants by the surface area, 11.2 cm.^2 .

Assuming a second-order rate law for the homogeneous solution reaction of mercury with iodine and making

(2) E. H. Klehr, "Solubility of Mercury in Organic Liquids," Ph.D. Thesis, Iowa State University, 1959, p. 34.

(3) Reference 2, p. 52.

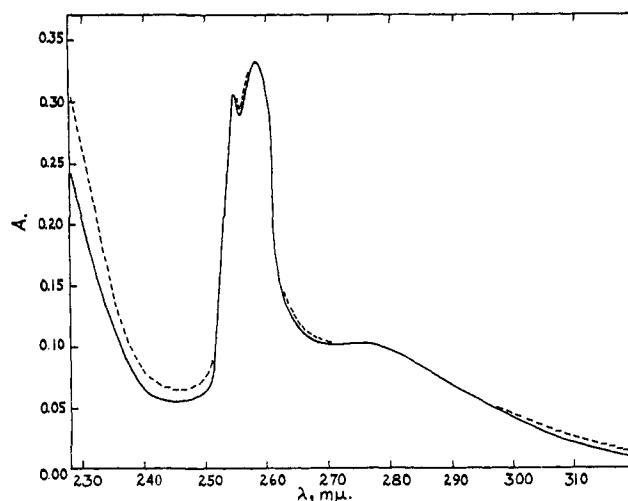


Fig. 2.—The product spectrum for the reaction of mercuric iodide in isoöctane with mercury at 25° : —, determined with a recording spectrophotometer using 10-cm. cells; calculated spectrum for $5.06 \times 10^{-6} M \text{ Hg}^0$ and $1.8 \times 10^{-6} M \text{ HgI}_2$, - - -.

the steady state approximation for mercury in solution, it is readily shown that Hg^0 does not accumulate in solution at 25° , given the present rate constants. Thus the rate of consumption of iodine by the homogeneous solution reaction with mercury is governed almost entirely by the rate of solution of the mercury. Since k_1^{Hg} is approximately temperature independent while k_2 presumably increases with temperature, it is likely that this is true at higher temperatures as well.

Reaction of Mercuric Iodide.—Mercuric iodide in isoöctane solution reacts with metallic mercury to give a greenish yellow solid which at first accumulates at the surface and then drifts away. This material blackens on exposure to light. It gives mercuric iodide solutions when washed with methanol, leaving behind a black deposit. It was assumed to be mercurous iodide. Kolthoff and Okinaka⁴ have shown that mercurous iodide can accumulate at a mercury surface.

After centrifuging out traces of the solid, the product solutions from the reaction of mercuric iodide with mercury showed a low intensity mercuric iodide spectrum in addition to the spectrum of elementary mercury. A typical example of such a product spectrum is shown in Fig. 2. The reaction is, therefore, appreciably reversible and the equilibrium concentration of mercuric iodide at 25° (which is the reciprocal of the equilibrium constant, since the product and the other reactant have unit activity) is $\sim 2 \times 10^{-6} M$.

The rate of consumption of mercuric iodide is accurately governed by a first-order rate law at all temperatures, with stirring rates of either 400 or 600 r.p.m. There is no apparent inhibition by mercurous iodide.⁴ A typical plot is shown in Fig. 3. Rate constants, $k_1^{\text{HgI}_2}$, obtained from such plots are shown in Table II. (The slope of plots like that shown in Fig. 3 gives $k_1^{\text{HgI}_2}$ directly, in spite of the fact that the reaction is appreciably reversible, because the reverse reaction must be of the zeroth order in order to give the proper form to the equilibrium constant. The mathematics is identical with that shown in eq. 6 and 7.) A few of these were obtained by starting with solutions of mercuric iodide in isoöctane. Most were obtained by following the disappearance of mercuric iodide produced *in situ* by the reaction of iodine with mercury. There seemed to be no difference between constants obtained in the two different ways. All of these rates are probably propor-

(4) I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **83**, 47 (1961).

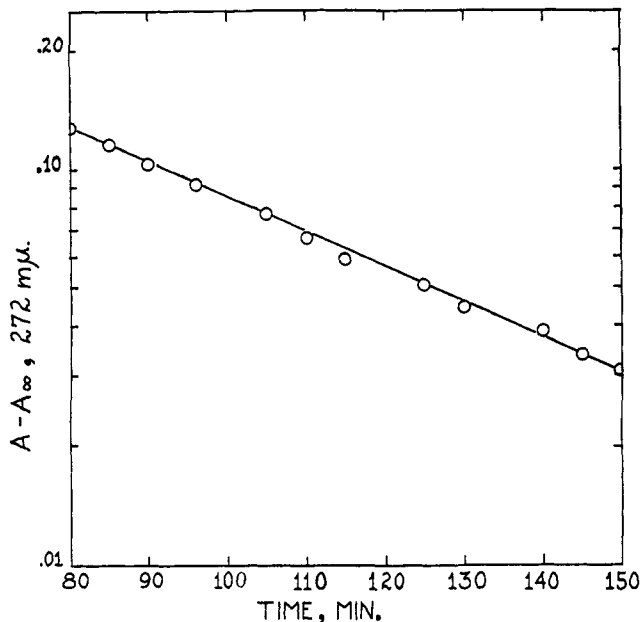


Fig. 3.—The log of the optical density as a function of time at 272 $m\mu$ and a stirring rate of 400 r.p.m. in isoöctane as a solvent in the presence of 17.6 g. of mercury. This reaction was initiated by allowing an $8 \times 10^{-5} M$ solution of I_2 to react with the mercury. At 80 minutes I_2 was no longer detectable in solution.

tional to the exposed surface area of the mercury. Mercuric iodide does not react with mercury in homogeneous solution in the absence of liquid mercury. This system will be discussed in a future publication.

TABLE II

RATE OF CONSUMPTION OF MERCURIC IODIDE		
Temp., °C.	Stirring rate, r.p.m.	$10^4 k_1 \text{HgI}_2$, sec. ⁻¹
0	600	4.7
25	600	4.5 ± 1.1
25	600	5.5 ± 0.5^a
25	600	3.2^b
40	600	5.1 ± 1.0
55	600	6.2 ± 1.3
70	600	5.8 ± 0.9
70	600	5.6 ± 0.4^a
70	600	7.2 ^c
25	400	3.0 ± 0.1^b
25	780	4.5 ^b

^a Another reaction vessel and stirrer. ^b Still another reaction vessel. ^c Mercuric iodide was the original starting material.

Reactions of Iodine.—At stirring rates above 200 r.p.m. the rate of disappearance of iodine from isoöctane is independent of the iodine concentration up to about 60–70% of completion. It obeys a first-order rate law very poorly. Figure 4 shows the iodine concentration as a function of time in a typical experiment. The derived zeroth-order rate constants, $k_0^{I_2}$, however, are proportional to the initial iodine concentration after the homogeneous solution rate has been subtracted from the total rate. The over-all rate can be represented by eq. 8. Plots of $k_0^{I_2}$ vs. $(I_2)_0$ were linear with intercepts equal to the previously measured rates of solution of mercury, k_0 , within the experimental uncertainty. The slopes of such plots, $k_1^{I_2}$, were evaluated by the method of least squares⁵

$$k_0^{I_2} = k_0 + k_1^{I_2}(I_2)_0 \quad (8)$$

for a variety of temperatures at 600 r.p.m. The stand-

(5) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industries," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 36–40.

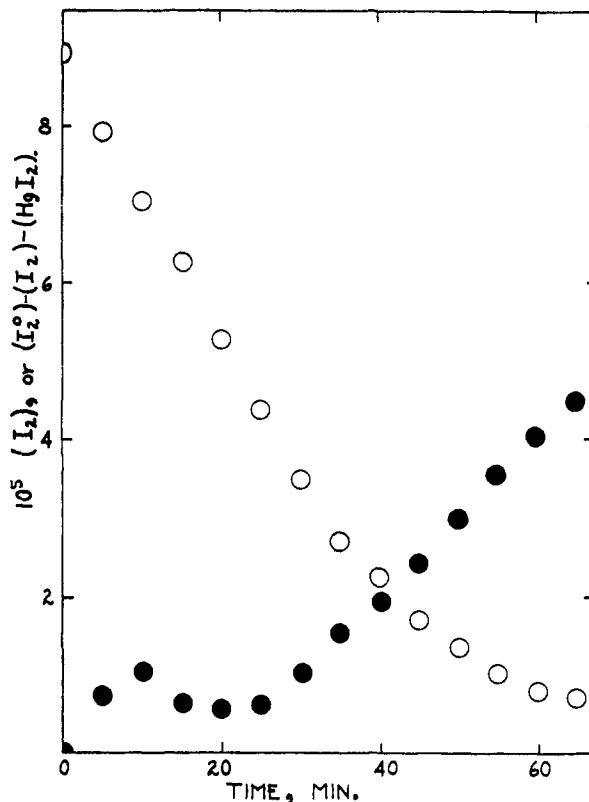


Fig. 4.—Iodine concentration and mercurous iodide build-up as a function of time in a typical experiment: iodine concentration, O; ●, $(I_2)_0 - (I_2) - (HgI_2)$, which is the number of moles of Hg_2I_2 present divided by the volume of the solution. The experiment was conducted at 25° and 600 r.p.m.

ard 17.6-g. mercury sample was used throughout. Measured rates of solution of mercury were included as points in evaluating the least squares slopes. The results are shown in Table III.

TABLE III

RATE OF REACTION OF IODINE WITH MERCURY			
Temp., °C.	$10^4 k_1^{I_2}$, sec. ⁻¹	$10^4 \times$ uncertainty, sec. ⁻¹	
		^a	^b
0	4.32	0.20	0.61
25	5.36	.10	.27
40	5.16	.28	.74
55	3.55	.19	.49
70	3.86	.02	.06

^a 50% confidence limits. ^b 90% confidence limits.

By evaluating both the iodine and mercuric iodide concentrations in solution, the amount of precipitated mercurous iodide can be calculated. This is also shown as a function of time in Fig. 4. The mercurous iodide begins to build up significantly at about the same time that deviations from the zeroth-order rate law begin. In a separate experiment mercuric iodide was allowed to reach equilibrium with a 17.6-g. sample of mercury, most of the solution above the mercury and precipitated mercurous iodide was removed, and a 150-ml. solution of $5 \times 10^{-5} M$ iodine was added. The resulting reaction was too fast to follow and was 70% complete in 17 seconds. It can then be assumed that mercurous iodide reacts with iodine as fast as it is formed from the mercuric iodide during most of the course of the reaction. If the rate of reaction of iodine with the metallic mercury is directly proportional to the iodine concentration, the over-all rate law would be that shown in eq. 9. However, if $k_1^{I_2}$ and $k_1^{HgI_2}$ are the same, eq. 9 reduces to eq. 8 since $(I_2) + (HgI_2) = -d(I_2)/dt = k_0 + k_1^{I_2}(I_2) + k_1^{HgI_2}(HgI_2)$ (9)

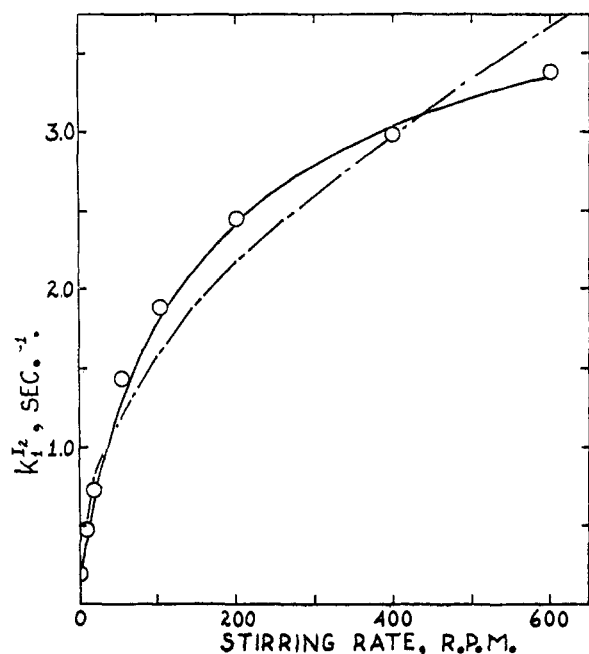


Fig. 5.—The rate of reaction of I_2 with a 17.6-g. sample of mercury as a function of the stirring rate. The initial concentration of I_2 was $9 \times 10^{-5} M$. The ordinate is $k_1^{I_2}$ regardless of whether it was obtained from a first-order rate law or derived from a more complicated behavior described. The solid line shows the value of $k_1^{I_2}$ calculated from eq. 11. The dashed line is $(0.20 + 0.14R^{1/2}) \times 10^{-4}$.

$(I_2)_0$ as long as the mercurous iodide does not accumulate. Comparison of Tables II and III shows that $k_1^{HgI_2}$ and $k_1^{I_2}$ are very similar.

Equation 9 implies that the reaction of iodine with mercury should be catalyzed by mercuric iodide. Table IV shows $k_0^{I_2}$ as a function of initial mercuric iodide concentration. The temperature was 25° , the stirring rate was 600 r.p.m. and the initial iodine concentration was about $8 \times 10^{-5} M$. Under these conditions, if $k_1^{HgI_2}$ and $k_1^{I_2}$ are equal, the rate should be governed by eq. 10. Table IV shows that the $k_1^{I_2}$,

$10^4(HgI_2)_0, M$	$10^3k_0^{I_2}, \text{mole/l. sec.}$	$10^4k_1^{I_2}, \text{sec.}^{-1}$
0.00	4.6	5.2
.11	3.8	3.8
.43	6.7	4.4
.80	7.0	4.5
1.14	6.5	2.9

derived from eq. 10, is constant and within experimental error identical with that obtained in the absence of added mercuric iodide up to near the solubility of mercuric iodide in isoöctane

$$-d(I_2)/dt = k_0^{Hg} + k_1^{I_2}[(I_2)_0 + (HgI_2)_0] \quad (10)$$

(the last value in Table IV). As this limit is approached, $k_0^{I_2}$ approaches a constant value and the apparent $k_1^{I_2}$ decreases accordingly. At the highest mercuric iodide concentrations eq. 10 is probably upset by the precipitation of mercuric iodide soon after the reaction begins.

From the temperature dependence of $k_1^{I_2}$ it is possible to derive an enthalpy of activation, ΔH^\ddagger . This was done, using eq. 11 and the method of least squares⁵ with the data in Table III. The value is $-1.0 \text{ kcal. mole}^{-1}$

$$R \ln (k_1^{I_2}/T) = \Delta H^\ddagger/T + C \quad (11)$$

if all the data are used and $-2.5 \text{ kcal. mole}^{-1}$ if the 0° datum is omitted, as there is reason to do. The latter

value has 50% confidence limits of $0.4 \text{ kcal. mole}^{-1}$ and 90% confidence limits of $1.4 \text{ kcal. mole}^{-1}$.

At low stirring rates (<200 r.p.m.) the rate of disappearance of iodine from isoöctane is first order in iodine and strongly dependent on the stirring rate. First-order rate constants, $k_1^{I_2}$, were obtained graphically. Figure 5 shows $k_1^{I_2}$ as a function of stirring rate at constant initial iodine concentration and mercury sample size at 25° .

First-order rate constants were measured at four temperatures between 25 and 70° with very little agitation. (There was no stirring except for three revolutions just before each sample was withdrawn in order to make the solution relatively homogeneous, so that a representative sample might be obtained.) Under these conditions most transport is probably due to convection. The rate constants are shown in Table V. From these rate constants, an activation energy, ΔH^\ddagger , of $6.2 \pm 0.8 \text{ kcal. per mole}$ was derived by the method of least squares from eq. 11.

$T, ^\circ C.$	25	40	55	70
$10^4k_1^{I_2}, \text{sec.}^{-1}$	0.19	0.32	0.53	0.93

At 400 r.p.m., 25° , and an initial iodine concentration of $9 \times 10^{-5} M$, $k_1^{I_2}$ in isoöctane varies as the square root of the weight of the mercury samples used, as shown in Table VI.

Wt. Hg, g.	$10^3k_1^{I_2}, \text{sec.}^{-1}$	$10^3k_1^{I_2}/\sqrt{\text{wt. Hg}}$
2.21	1.06	7.1
5.41	1.78	7.6
10.14	2.29	7.2
17.65	2.98	7.3
35.10	4.9	8.3

In the limit the upper surface of a small segment of a large sphere has an area, A , of $2(\pi r V)^{1/2}$. Since the experiments were conducted in a round-bottom flask of fixed radius, r , and the volume of the mercury, V , is directly proportional to its mass, this finding strongly suggests the reasonable conclusion that the rate is proportional to the surface area and that our mercury samples have the shape of segments of spheres. Visually they appear to have such a shape (more nearly so in the presence than in the absence of isoöctane).

Reaction with Aqueous Solutions.—A similar investigation was conducted using aqueous iodine and mercuric iodide solutions. The results obtained were qualitatively and quantitatively similar to those in isoöctane except that initial rates proved to be irreproducible so that rate constants were obtained from points corresponding to 50% reaction. At 25° , 600 r.p.m., with a 17.5-g. mercury sample $k_1^{HgI_2}$ was 2.6×10^{-4} and $k_1^{I_2}$ was $(6.8 \pm 1.2) \times 10^{-4}$.

Reproducibility.—One of the principal reasons for using the liquid metal, mercury, in the present study was the hope that it would give precise and readily reproducible results. Examination of the foregoing results reveals that this was not entirely achieved. In extreme cases random variations of nearly a factor of two were obtained on remeasuring the same quantity. These discrepancies were particularly marked if the apparatus used was changed or if a long time period elapsed between determinations. As a result we have tried to avoid basing any conclusions on small differences in rates and have in no case based any conclusion on a single determination of a rate constant. It will also be noted that somewhat different values of the

same constant appear in several of the figures and tables. When this is true the value which appears is the most nearly contemporaneous to others in that particular comparison or is the one measured under most nearly identical conditions.

Discussion

The first point of interest in this discussion is the relative importance of transport processes and chemical processes in determining the rates of the surface reactions. The foregoing data do not provide a completely conclusive answer; however, the following considerations strongly suggest that $k_1^{I_2}$ in isoöctane at 600 r.p.m. is nearly independent of the rates of transport processes.

1. Assuming that two consecutive steps, transport to the surface and reaction at the surface, are involved in the over-all kinetics, eq. 11a gives the over-all rate constant.⁶ The rate constant for transport is k_t

$$k_1^{I_2} = k_c k_t / (k_c + k_t) \quad (11a)$$

and that for reaction at the surface is k_c . Values of k_c , $4.15 \times 10^{-4} \text{ sec.}^{-1}$, and k_t , $(2 \times 10^{-5} + 2.78 \times 10^{-6} R) \text{ sec.}^{-1}$ (where R is the stirring rate), gave an excellent fit to the observed rate constants, as shown in Fig. 4 (the solid line). The value of k_t was obtained by fitting the data at very low stirring rates. At 600 r.p.m., k_t , $1.69 \times 10^{-3} \text{ sec.}^{-1}$, is very close to the observed value of $k_1^{I_2}$, $1.4 \times 10^{-3} \text{ sec.}^{-1}$. The value of k_c was then chosen so as to give an optimum fit for all the data. It is only 25% larger than the observed $k_1^{I_2}$ at 600 r.p.m.

It has been shown⁶ that eq. 12 governs the rate constants of reactions in stirred systems when these are entirely limited by the rates of transport processes. In eq. 12, C and α are arbitrary constants, the latter said to vary between 0.5 and 1.0.⁶

$$k_t = CR^\alpha \quad (12)$$

This is consistent with the form given to k_t empirically (C , 2.78×10^{-6} , and α , unity) provided that a small constant is added (presumably due to diffusion and convection). A poorer approximation to $k_1^{I_2}$ is obtained if α is taken substantially less than unity and $k_c \gg k_t$ (Fig. 5 shows the best fit to be obtained with $\alpha = 0.5$). However, Fig. 5 plainly does not exclude numerical values of C and α somewhat different from those taken.

2. The rate constant for reprecipitation of mercury, k_1^{Hg} , is larger by about a factor of three than $k_1^{I_2}$ at 25° and 600 r.p.m. Rates of transport processes for molecules of the same molecular weight should be very similar^{6,7} and the molecular weight of iodine (254) is very similar to the atomic weight of mercury (201). It follows that the slower process must be retarded by non-transport (chemical) considerations. The difference would seem to be well outside of the combined uncertainties of the two values as both are the averages of several determinations. As pointed out above, k_1^{Hg} at 25° and 600 r.p.m. is nearly identical with the value of k_t under the same conditions as obtained from the variation in $k_1^{I_2}$ with stirring rate. These observations suggest that the rate of precipitation of mercury is controlled by the transport process and that C and α are roughly correct.

3. Mercuric iodide is formed at the surface and carried away without an appreciable lag. Mercuric iodide is also able to react with the surface at about the same rate as iodine. The transport process that carries mercuric iodide away from the surface has the same rate constant as that which brings it up to the surface and both are probably a little smaller than those for the transport of iodine. The fact that transport of mercuric iodide away from the surface competes with reac-

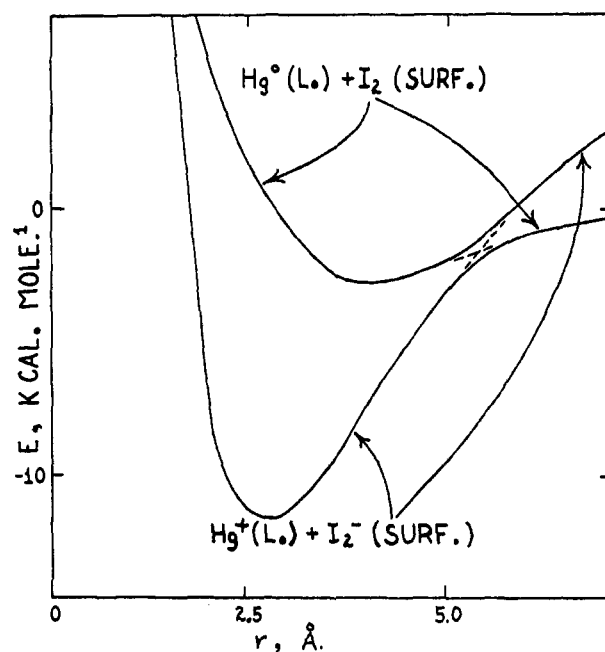


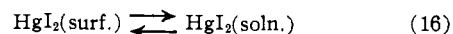
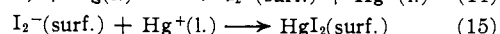
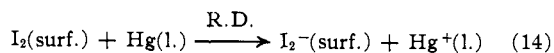
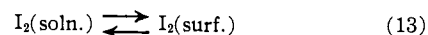
Fig. 6.—A suggested semiquantitative plot of potential energy, E , vs. r , the distance of the iodine molecule from the surface of the mercury. At large separation the $Hg^0(l.) + I_2(soln.)$ is more stable. In the adsorbed state $Hg^+(l.) + I_2^-(surf.)$ is more stable. At an intermediate r there is a "cross-over." The energy of the less stable arrangement is also shown. The zero of energy is $Hg^0(l.) + I_2(soln.)$. The minimum of energy shown for $Hg^+(l.) + I_2^-(surf.)$ is a rough estimate.

tion with the surface strongly suggests that $k_t > k_c$ for iodine also.

4. Rates of transport processes usually have small but positive activation enthalpies in the range of 2.8–6.5 kcal. mole⁻¹.⁶ With just enough stirring to avoid sampling problems, $k_1^{I_2}$ is surely determined almost solely by the transport process. Under those conditions ΔH^\ddagger is 6 kcal. mole⁻¹. At 600 r.p.m., however, a negative activation enthalpy is obtained, particularly if the 0° datum is neglected. It seems likely that the ΔH^\ddagger obtained by neglecting the 0° datum is the more closely associated with k_c , because k_t undoubtedly has a positive ΔH^\ddagger , which would make $k_1^{I_2}$ a poorer measure of k_c at the lowest temperature than at the others. In any event, if ΔH^\ddagger is systematically in error due to the composite nature of $k_1^{I_2}$ it must be too positive. This, combined with the error discussion given above, makes it seem very unlikely that the true value of ΔH^\ddagger at 600 r.p.m. is as high as +2 kcal. mole⁻¹. Some process capable of giving a negative activation enthalpy is required.

In aggregate these arguments seem convincing. The following theory, however, does not rest on the requirement that $k_1^{I_2}$ equal k_c but only that they are of the same order of magnitude.

A mechanism capable of accommodating the observed behavior of $k_1^{I_2}$, particularly the negative activation enthalpy, is shown in eq. 13–16.



The postulated rate-determining step, shown in eq. 14, is an electron transfer from one of the conduction bands of the mercury to an unfilled orbital of the iodine molecule.

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

(7) C. V. King, *Trans. N. Y. Acad. Sci.*, **10**, Series 2, 262 (1948).

The transition state theory expression for the rate constant of a surface reaction is shown in eq. 17,⁸ in which v is the solution volume, a is the surface area, k is

$$\frac{v}{a} k = \mathcal{K} \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (17)$$

a pseudo-first-order rate constant, \mathcal{K} is the transmission coefficient, ΔS^\ddagger is the entropy, and ΔH^\ddagger is the enthalpy of activation.

A plot of potential energy *vs.* distance of the iodine from the mercury surface is shown in Fig. 6. The latter, to a good approximation, is the reaction coördinate. The internuclear distance at which the energy of $\text{Hg}^0(1.) + \text{I}_2(\text{soln.})$ just equals that of $\text{Hg}^+(1.) + \text{I}_2^-(\text{soln.})$ can be calculated from eq. 18 and 19.

$$E_{\text{Hg}^0(1.)} + E_{\text{I}_2(\text{soln.})} - E_{\text{Hg}^+(1.)} - E_{\text{I}_2^-(\text{soln.})} = 0 \quad (18)$$

$$E_{\text{Hg}^+(1.)} + E_{\text{I}_2^-(\text{soln.})} = \Phi_{\text{Hg}} - A_{\text{I}_2} - \frac{e^2}{r_c D} + e_{\text{I}_2^-} \quad (19)$$

In these equations E is an energy. The energy of liquid mercury and iodine at unit activity in the gas phase are taken as zero. The energy of iodine in solution is small and was approximated by the standard enthalpy of solution from the vapor, -4 kcal. mole⁻¹.^{9,10} The work function of mercury, Φ_{Hg} , is 105 kcal. mole⁻¹,¹¹ and the electron affinity of molecular iodine in the vapor phase, A_{I_2} , can be estimated as 55 kcal. mole⁻¹.^{12,13} The energy of solution of I_2^- , $e_{\text{I}_2^-}$, was -23 kcal. mole⁻¹, approximated by the Born changing energy,¹⁴ using the optical dielectric constant of isoöctane,¹⁵ D , 1.94. The charge on an electron, 4.80×10^{-10} e.s.u., is e . The value obtained for r_c is 5.5 Å. This value is fairly insensitive to the value used for the dielectric constant, as this enters the $e^2/r_c D$ term and $e_{\text{I}_2^-}$ in compensating ways. Although the interpretation of this distance is not altogether unambiguous, its general size is probably realistic. At no time after the iodine comes into the near neighborhood of the mercury so that it would be called $\text{I}_2(\text{surf.})$ does its energy rise above its energy in the bulk of the solution so that a negative value of ΔH^\ddagger is expected.

If partition functions can be estimated, the entropy of activation can be calculated from eq. 20,¹⁶ in which Q^\ddagger is the partition function of the transition state and Q is the product of the partition function of iodine in solu-

$$\Delta S^\ddagger = R \ln(Q^\ddagger/Q) - RT \frac{d}{dT} \ln(Q^\ddagger/Q) \quad (20)$$

tion and that of liquid mercury. The partition function of the transition state could not be reliably estimated from first principles, but an upper limit for the ratio of partition functions can be.

Electron transfer is likely only when the energies of the products and reactants shown in eq. 14 are approximately equal, because otherwise a photon would have to be adsorbed or emitted.¹⁷ Since the energy of the products strongly depends on the length of the charge separation, the translational mode perpendicular to the surface of the mercury becomes the reaction coördinate and one degree of translational freedom is lost in forming the transition state.⁸ The iodine at this point is

assumed to be free to move parallel to the mercury surface; thus the other two degrees of translational freedom are assumed to be unchanged.

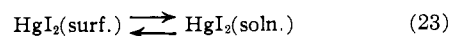
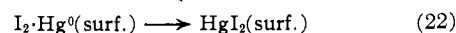
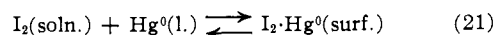
The nature of the empty orbital of iodine to which the electron is transferred is not known and, consequently, the preferred orientation of the iodine to the mercury surface is not known; presumably it is either that in which the iodine-iodine axis is perpendicular to the mercury surface or parallel to it. In the former case both rotational degrees of freedom would be converted to vibrations; in the latter case only one would be. The latter seems more likely and was assumed correct.¹²

The translational partition function for iodine in isoöctane solution, f_T , was estimated from the vapor phase partition function by assuming that the small, negative, entropy of solution of iodine from the vapor (-3.2 cal. mole⁻¹ deg.⁻¹ when concentrations are expressed in moles l.⁻¹ in both phases)^{9,10} is entirely due to a loss of translational freedom. This gives f_T a value of 9.0×10^8 cm. in isoöctane solution. The rotational partition was assumed to have the gas phase value in solution, also. The new vibration was assumed to have a frequency of 100 cm.⁻¹. With these approximations standard equations¹⁸ give a value of -46.5 cal. mole⁻¹ deg.⁻¹ for ΔS^\ddagger .

The treatment of the translation follows that of Glasstone, Laidler and Eyring,⁸ and is plainly more reliable than that for rotation and vibration. Fortunately, the former is the largest contributor to ΔS^\ddagger (-41.0 cal. mole⁻¹ deg.⁻¹).

Using -46.5 cal. mole⁻¹ deg.⁻¹ for ΔS^\ddagger , -1.0 kcal. mole⁻¹ for ΔH^\ddagger and the observed rate constant, along with the known volume and area, eq. 17 gives $\sim 10^{-4}$ for \mathcal{K} . If -2.6 kcal. mole⁻¹ is used for ΔH^\ddagger \mathcal{K} is $\sim 10^{-5}$. Transmission coefficients substantially less than unity are not unreasonable for electron transfer reactions,^{13,18-23} but it does seem unreasonable that \mathcal{K} should be so small for a reaction with a cross-over distance of only 5-6 Å.^{13,19} In order to accommodate a transmission coefficient in the range 10^{-1} to 10^{-3} , a ΔS^\ddagger of about -65 cal. mole⁻¹ deg.⁻¹ is required instead of the -47 cal. mole⁻¹ deg.⁻¹ calculated above. The additional negative entropy is most easily introduced by assuming a small restriction on the lateral movement of the iodine along the mercury surface. Indeed, \mathcal{K} could be raised all the way to unity by this device.

An alternative mechanism that could accommodate the negative activation enthalpy is shown in eq. 21-23. In the first step of this mechanism it is proposed that



iodine is chemisorbed with a large, negative enthalpy. In the second step it reacts through some "normal" process with a positive enthalpy of activation to give adsorbed mercuric iodide. If the enthalpy of activation in the second step is numerically smaller than the enthalpy of chemisorption, then the observed activation enthalpy would be negative.²⁴ However, the substantial negative enthalpy required in the first step would seem to suggest strong chemisorption. Since metallic mercury presents a very limited surface area, this, in

(8) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 351.

(9) D. A. Shirley and W. F. Glauque, *J. Am. Chem. Soc.*, **81**, 4778 (1959).

(10) J. H. Hildebrand and D. N. Glew, *J. Phys. Chem.*, **60**, 618 (1956).

(11) W. B. Hales, *Phys. Rev.*, **32**, 950 (1928).

(12) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(13) J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

(14) M. Born, *Z. Physik*, **1**, 45 (1920).

(15) C. P. Smyth, "Dielectric Behaviour and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 9.

(16) M. M. Kreevoy in "Investigation of Rates of Mechanisms of Reactions," S. L. Friess, E. S. Lewis and H. Weiseberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, Part 2, Chapter 23.

(17) E. U. Condon, *Am. J. Phys.*, **15**, 365 (1947).

(18) R. J. Marcus, B. J. Zwolinski and H. Eyring, *J. Phys. Chem.*, **58**, 432 (1954).

(19) Reference 8, p. 306.

(20) R. A. Marcus, "Transactions of the Symposium on Electrode Processes," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 239.

(21) L. Landau, *Physik. Z. Sowjetunion*, **2**, 46 (1932).

(22) (a) C. Zener, *Proc. Roy. Soc. (London)*, **A137**, 696 (1932); (b) C. Zener, *ibid.*, **A140**, 660 (1933).

(23) C. A. Coulson and K. Zalewski, *ibid.*, **A268**, 437 (1962).

(24) A. W. Adamson, "Physical Chemistry of Surfaces," Interscience Publishers, Inc., New York, N. Y., 1960, p. 546.

turn, would suggest a ready saturation of the surface, which would produce a steady diminution in $k_1^{1/2}$ as the initial iodine concentration was raised. No such effect is observed in the present reaction and mercury is not thought to present a surface on which strong chemisorption easily takes place.²⁵

It seems likely that aqueous solutions of iodine react with mercury *via* the same mechanism as the isoöctane solutions, but evidence is not conclusive.

Future work will explore the effect of other metals dissolved in the mercury, solvent effects and mechanisms for the reaction of other substrates with mercury. It is hoped that these studies will solve some of the problems raised in the present work.

Experimental

Materials.—Merck reagent grade iodine and Mallinckrodt analytical reagent grade mercuric iodide were used without further purification. Phillips Petroleum Co. spectro grade "isoöctane" was used with no treatment. Distilled water was used in the experiments involving aqueous solutions. Mercury was triply distilled material. Shortly after beginning this study, it was found that mercury which had been used in previous runs could be washed with methanol to remove the surface film. After being washed several times with methanol and then blotted dry with filter paper, the mercury appeared to be clean and give results indistinguishable from those obtained with fresh, unused mercury. This method of purification was then adopted for most of the subsequent work.

Apparatus.—The reaction vessel was a 200-ml. 3-neck round-bottom flask with standard taper 24/40 ground glass joints. The two side necks were stoppered with ground glass stoppers and the center one was fitted with a Tru-bore paddle stirrer. The bottom of the paddle blade, which was used with the flat edge down, was kept 15 mm. above the bottom of the flask. It was discovered that the geometry of the equipment was extremely critical, a variation in paddle height of a few millimeters sometimes leading to a large variation in the observed rate of reaction. A total of four different 200-ml. round-bottom flasks and two different Tru-bore stirrers were used in these studies.

The use of different stirring motors did not lead to any obvious change in rate. A fixed speed stirrer, operating at 200 and 400 r.p.m., was used for most of the work at these stirring speeds. A cone-drive motor, capable of variation in speed from 100 to over 1200 r.p.m., was used for most of the rest of the work. A variable-speed motor, geared down to 10 to 55 r.p.m., was used for the slow stirring rates. The runs with a rate reported as 0.1 r.p.m. were run with no stirring except for three revolutions

(25) J. C. P. Miguole, *J. Chem. Phys.*, **21**, 1298 (1953).

of the stirrer just before a sample was to be withdrawn in order to make the solution homogeneous. The samples were taken about every 30 minutes for the very slow reactions.

The reaction vessel was immersed in a water thermostat of conventional design maintained within $\pm 0.2^\circ$ of the nominal temperature.

Optical densities of solutions were measured in a 1-cm. quartz cell with a Beckman model DU spectrophotometer that had a thermostated cell compartment. Continuous ultraviolet spectra were measured with a Beckman model DK-2 recording spectrophotometer. Elementary mercury, mercuric iodide and iodine all have distinctive electronic spectra in isoöctane, as do the latter two in water.

Procedure.—The solution to be studied (150 ml.) was run into the 200-ml. flask which had been placed in a constant-temperature bath. It was stirred for at least 15 minutes while coming to thermal equilibrium. A 3-ml. sample was withdrawn, centrifuged, and the optical density determined at the appropriate wave lengths. The wave lengths used are listed in Table VII. The sample was then returned to the reaction flask. Initial iodine and mercuric iodide concentrations were calculated from the initial optical density measurements. The reaction was begun by stopping the stirrer, adding the weighed mercury sample and, after about 10 seconds, starting the stirrer. Samples were centrifuged to remove any suspended material (mercurous iodide).

TABLE VII

WAVE LENGTHS AND EXTINCTION COEFFICIENTS USED

Compound	$\lambda_{\text{max}}, \text{m}\mu$	ϵ_{max}
I ₂	523	900
HgI ₂	272	4200
Hg	257	5000

Samples withdrawn during the rate-of-solution studies on mercury at higher temperatures were not centrifuged since it was discovered that mercury came out of solution rapidly upon cooling. Subsequently, the sampling and spectrophotometric equipment was preheated at the temperature of the run, the cell compartment was maintained at the same temperature as the reaction, and the measurement was made as quickly as possible. Nevertheless, the rates of solution and reprecipitation at 70° were not very reproducible and are not considered as reliable as those at other temperatures.

Acknowledgments.—We are very much indebted to Drs. Bruckenstein, Reynolds, Lumry and Halpern for helpful suggestions. We are pleased to acknowledge the support provided by the Alfred P. Sloan Foundation through a fellowship to M. M. K.

[CONTRIBUTION NO. 1726 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

The Heat of the Reaction between Polyriboadenylic Acid and Polyribouridylic Acid^{1,2}

BY MARY A. RAWITSCHER, PHILIP D. ROSS³ AND JULIAN M. STURTEVANT

RECEIVED MARCH 6, 1963

Calorimetric measurements of the heat of interaction of polyriboadenylic acid (poly A) and polyribouridylic acid (poly U) in 0.1 M KCl at pH 7 and 10°, 25° and 40° are reported. The heat of reaction divided by the absolute temperature varies linearly with temperature over this range and gives on extrapolation a value of $\Delta H = -7600 \text{ cal. (mole of base pairs)}^{-1}$ at the melting temperature of the poly (A + U) formed. Calorimetric titrations of poly A from neutral to acid pH are interpreted to give tentative values for the heat of the coil-to-helix transformation of poly A, and these data are employed to correct the poly (A + U) heats for the apparent degree of order existing in the conformation of the poly A before the reaction. Extrapolation to the melting temperature of poly (A + U) of these revised values gives for the heat of interaction of random coil poly A with random coil poly U to form the 1:1 helical complex at pH 7 a value of approximately $-8700 \text{ cal. (mole of base pairs)}^{-1}$.

Introduction

The double helical structures of deoxyribonucleic acid (DNA) and of the complexes formed by the interaction of various synthetic polynucleotides are stabilized by forces the origin of which is not fully understood. It is therefore of interest to determine experimentally the energy changes accompanying the forma-

tion of these highly ordered structures from approximately random coil conformations of the constituent polymers. In this paper we report the results of calorimetric measurements of the heat effect accompanying the interaction of polyriboadenylic acid (poly A) with polyribouridylic acid (poly U) to form a complex, poly (A + U), of more highly ordered structure than either of the constituent polymers.⁴ Similar measure-

(1) A preliminary report of this work was presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) This work was aided by grants from the U. S. Public Health Service (RG-4725) and the National Science Foundation (G-9625).

(3) National Institutes of Health, Bethesda, Md.

(4) Preliminary calorimetric measurements of this reaction were performed in collaboration with Professor A. Rich of the Massachusetts Institute of Technology.