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IODODEMERCURATION OF (PENTAFLUOROPHENYL)- AND (PENTACHLOROPHENYL)MERCURY BROMIDES

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SUMMARY

Reaction of (perfluorophenyl)- and (perchlorophenyl)mercury bromides with iodine in DMF follows the first order which is discussed in terms of the $S_E1(N)$ mechanism. In benzene an analogous reaction proceeds only in the presence of iodide ions. In both solvents the reaction with I_3^- follows the second order kinetics. A mechanism is suggested in which iodinating agent plays the role of a nucleophilic catalyst, $S_E1(I_3^-)$.

INTRODUCTION

Earlier we found[1] that the mechanism of iododemercuration reaction in the series of organomercury compounds, R_2Hg, may change from S_E2 to $S_E1(N)$[2] if the compounds have strong electron accepting organic groups and in aprotic dipolar type solvents. It is known[3] that the asymmetric organomercury compounds RHgX possess better complexing ability with nucleophiles than the compounds R_2Hg. Hence it could be expected that iododemercuration of perfluoro- and perchloroderivatives, RHgX, might be performed in the appropriate solvents or with nucleophilic catalysts in accord with $S_E1(N)$ mechanism.

The present work is concerned with kinetics of the reaction of (pentafluorophenyl)- and (pentachlorophenyl)mercury bromides with iodide ion in dimethylformamide (DMF) and benzene. In case of C_6F_5HgBr the reaction in dimethylsulfoxide (DMSO) was also investigated.

EXPERIMENTAL

Kinetic investigation was conducted by spectroscopic method using an CF-4 instrument and thermostatted cuvettes by measuring the change in optical density of iodine (λ 430 nm in DMF and DMSO) or anion I_3^- (λ 390 nm at concentration 10^{-4} mole/l and λ 470 nm at concentration 10^{-3} mole/l in C_6H_6).

(Pentafluorophenyl)mercury bromide was obtained by the reaction of $(C_6F_5)_2$-Hg with $HgBr_2$[4], m.p. 155° (from CCl_4).

(Pentachlorophenyl)mercury bromide was obtained from $(C_6Cl_5)_2Hg$ and $HgBr_2$, m.p. >300° (from C_6H_6) by the method proposed by Dessy for the synthesis of C_6Cl_5HgCl[5], although it has been indicated that the reaction did not proceed[6]. (Found: C, 13.46; Hal, 48.19; Hg, 38.04. C_6BrCl_5Hg calcd.: C, 13.58; Hal, 48.49; Hg, 37.85%.)

DMF, DMSO and C_6H_6 were purified as described[7-9]. The same solvent portion was used in the series of measurements.

Preparative separation of the reaction products

Reaction of C_6F_5HgBr with I_3^- in benzene. A solution of 0.02 mole of organomercury compound and I_3^- in benzene (using tetradecylammonium iodide as a source of iodide ions) was kept in dark until the disappearance of the colour of iodine. Solvent was evaporated *in vacuo* (10 mm) and the residue extracted with cold chloroform. Evaporation of $CHCl_3$ gave perfluoroiodobenzene (80%), b.p. 60–60.5° (25 mm), $n_D^{21.5}$ 1.4940, UV spectrum in EtOH: λ_{max} 226,260 nm [lit.data[10].: b.p. 159–160° (760 mm), 60–60.5° (25 mm) $n_D^{19.5}$ 1.4965, UV spectrum in EtOH λ_{max}226,252 nm)]. Inorganic mercury salt (85%) was isolated from insoluble part.

Reaction of C_6Cl_5HgBr with I_3^- in benzene. The primary operations were similar to those mentioned above. The residue was treated with cold methanol to separate inorganic mercury salt and $(C_{10}H_{21})_4NI$. Pentachloroiodobenzene thus isolated was recrystallized from methanol; (80%), m.p. 208° (lit.data[11]: m.p. 211°).

Kinetic GLC study of the accumulation of pentafluoroiodobenzene

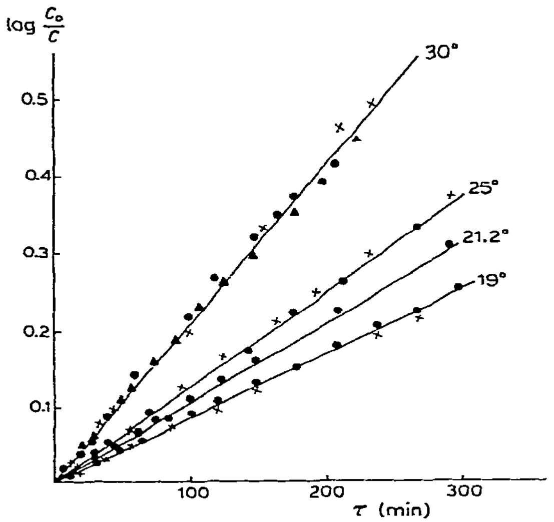
Iododemercuration of C_6F_5HgBr in DMF at 30° was conducted at reagent concentrations of 1×10^{-2} mole/l. The 1 ml portions withdrawn from the reaction mixture were added to 1 ml of aqueous 0.1 *N* $Na_2S_2O_3$ solution. Then 5 ml of water was added to the mixture, pentafluoroiodobenzene was extracted with 3 ml of hexane. Detailed experiments showed that with such a treatment, C_6F_5I could be completely removed from DMF/water phase to hexane solution. For a complete separation of DMF, the solution was washed twice with a saturated NaCl solution and dried over anhydrous $MgSO_4$. Chromatographic analysis was carried out using a Chrom-2 instrument with a flame-ionization detector [column twin-60(12%) on chromosorb W (80/100 mesh), length 2.35 m, ∅ 4 mm, column temp. 120°, nitrogen as carrier gas at a rate of 40 ml/min, mesitylene as internal standard].

RESULTS

Iododemercuration in DMF

Iododemercuration of (pentafluorophenyl)mercury bromide in DMF was investigated at equimolar reagent concentrations within 0.25×10^{-3}–1×10^{-3} mole/l at temperatures 19, 21.2 and 30°. Temperature was maintained with an accuracy of ±0.1°. Optical density of the solution changed instantaneously on mixing the solutions of organomercury compound and iodine. Probably it was as a result of interaction between I_2 and C_6F_5HgBr [at $C_0 = 0.5 \times 10^{-3}$ mole/l and λ 430 nm, $D_0 = 0.820$, D_0 (reaction mixture) $= 0.556$].

Thus the starting values D_0 were found by extrapolating $D = f(\tau)$ to a zeroth time. The values D_0 obtained for various starting concentrations obey the Lambert–Beer law. The reaction followed the first order kinetics, the first order rate constants which can be seen from anamorphoses of kinetic curves in logarithmic coordinates (Fig. 1) keep well within all region of the kinetic curve, and show rather good coinci-



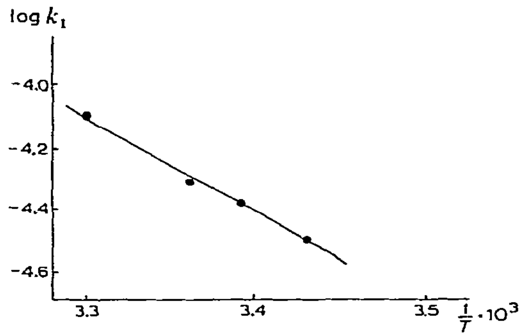


Fig. 1. Dependence log $C_0/C = f(\tau)$ for reaction of C_6F_5HgBr with I_2 in DMF at various temperatures (× $C_0 = 0.25 \times 10^{-3}$ mole/l, ● $C_0 = 0.5 \times 10^{-3}$ mole/l, ▲ $C_0 = 1.25 \times 10^{-3}$ mole/l).

Fig. 2. Dependence log $k_1 = f(1/T)$ for reaction of C_6F_5HgBr with I_2 in DMF.

TABLE 1

$C_6F_5HgBr + I_2$, DMF			$C_6Cl_5HgBr + I_2$, DMF		
Temp. (°C)	$C_0 \times 10^3$ (mole·l^{-1})	$k_1 \times 10^5$ (sec^{-1})	Temp. (°C)	$C_0 \times 10^3$ (mole·l^{-1})	$k_1 \times 10^5$ (sec^{-1})
19	0.5	3.38	20.3	0.5	1.30
	0.25	3.18	25	1.0	2.00
				0.5	2.00
21.2	0.5	4.15		0.25	1.90
25	0.5	4.44	30	0.5	2.40
	0.25	4.75		0.25	2.38
30	1.25	8.61	50	0.5	9.45
	0.5	8.90		0.25	9.60
	0.25	8.60			

dence at different concentrations. The data obtained are summarized in Table 1.

The relationship log $k_1 = f(1/T)$ is shown in Fig. 2. Enthalpies and entropies of activation are $\Delta H^{\neq} = 14.1 \pm 0.3$ kcal/mole, and $\Delta S^{\neq} = -33.4$ e.u., respectively.

Addition of mercury bromide to the reaction mixture decreases the reaction rate. With an equimolar amount of $HgBr_2$ the first order rate constant is 4.5×10^{-5} sec^{-1} (30°) *i.e.* half as compared to the value of k_1 without $HgBr_2$.

(Pentachlorophenyl)mercury bromide was allowed to react with iodine in DMF in the same concentration range and at temperatures 20.3, 25, 30, 50°. Change of optical density of the iodine solution after addition of C_6Cl_5HgBr was essentially weaker [at $C_0 = 0.5 \times 10^{-3}$ mole/l, 20°, $\lambda = 430$ nm, $D_0 = 0.820$, D_0(reaction mixture) = 0.691] but still noticeable, thus D_0 has been found from extrapolation. The reaction

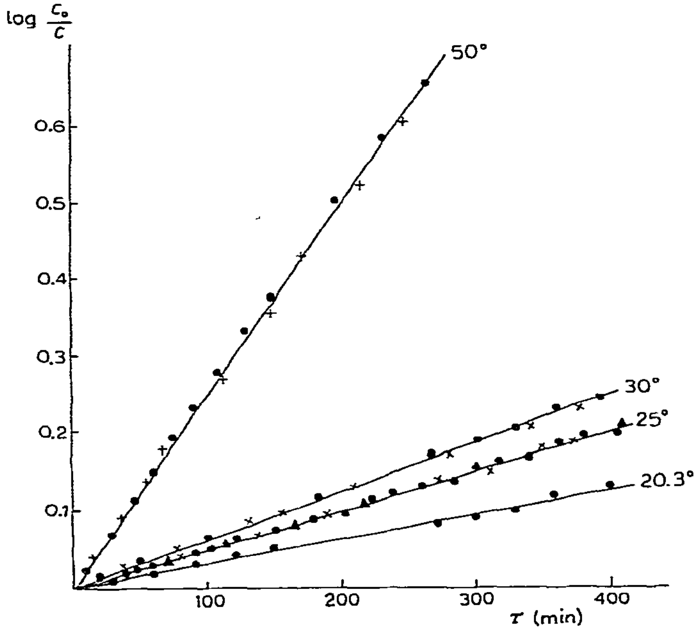


Fig. 3. Dependence log $C_0/C = f(\tau)$ for reaction of C_6Cl_5HgBr with I_2 in DMF at various temperatures (× $C_0 = 0.25 \times 10^{-3}$ mole/l, ● $C_0 = 0.5 \times 10^{-3}$ mole/l, ▲ $C_0 = 1 \times 10^{-3}$ mole/l).

rate constant keeps its value in calculation employing the first order equation (Table 1).

Anamorphoses of kinetic curves log $C_0/C = f(\tau)$ for various temperatures are shown in Fig. 3.

Thermodynamic factors were found from the temperature dependence of the reaction rate (Fig. 4): $\Delta H^{\neq} = 11.8 \pm 0.3$ kcal/mole. $\Delta S^{\neq} = -45.2$ e.u.

Iododemercuration reactions of (pentafluorophenyl)- and (pentachlorophenyl)-mercury bromides were conducted in DMF in the presence of iodine and equimolar amount of potassium iodide. It is known that in the presence of iodide ion in DMF the iodine I_3^- forms complex, $K = 1.05 \times 10^7$ l/mole[12]. Addition of organomercury compound to such a solution resulted in a sharp decrease in optical density of the solution, which was most significant in case of C_6F_5HgBr. For example, at a concentration of 0.5×10^{-3} mole/l, $t = 30°$, $\lambda = 430$ nm, the value of D_0 decreased from 1.5 to 1.2 and 0.795 for C_6Cl_5HgBr and C_6F_5HgBr, respectively. Thus the starting values D_0 were determined from an extrapolation of the $D = f(t)$ plot to a zeroth value of time. Such optical density change is apparently due to the formation of a complex $RHgX \cdot I_3^-$. It was shown that on varying the equimolar concentrations of organomercury compound and I_3^- the D_0 obeys the Lambert–Beer law.

Both the reactions are of second order in the presence of iodide ion, the second order rate constant being satisfactorily maintained either in the course of kinetic curves or at the various reagent concentrations.

The results obtained for both the reactions are listed in Table 2.

Anamorphoses of kinetic curves in the $1/C_0(C_0/C - 1) - \tau$ coordinates are shown in Figs. 5 and 6. The estimated approximate thermodynamic reaction factors

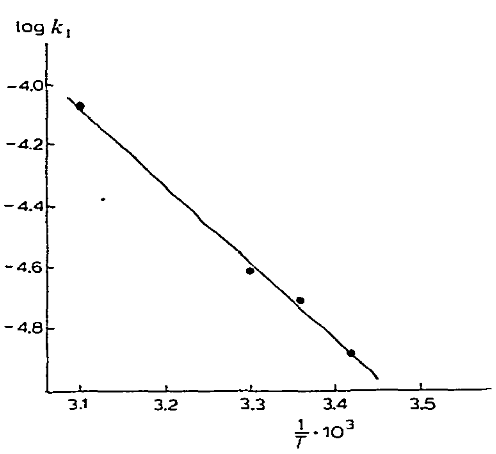


Fig. 4. Dependence log $k_1 = f(1/T)$ for reaction of C_6Cl_5HgBr with I_2 in DMF.

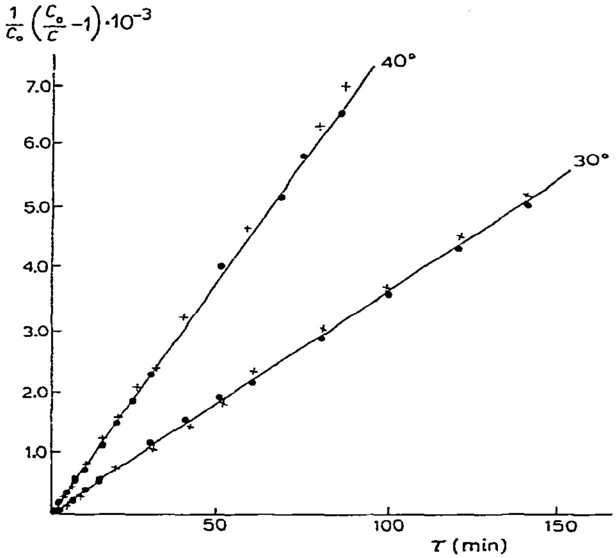


Fig. 5. Dependence $1/C_0(C_0/C-1) = f(\tau)$ for reaction of C_6F_5HgBr with I_3^- in DMF at various temperatures (× $C_0 = 0.25 \times 10^{-3}$ mole/l, ● $C_0 = 0.5 \times 10^{-3}$ mole/l).

TABLE 2

$C_6F_5HgBr+I_3^-$, DMF			$C_6Cl_5HgBr+I_3^-$, DMF		
Temp. (°C)	$C \times 10^3$ (mole·l^{-1})	k_2 (l·mole^{-1}·sec^{-1})	Temp. (°C)	$C \times 10^3$ (mole·l^{-1})	k_2 (l·mole^{-1}·sec^{-1})
30	0.50	0.59	26	1.00	0.13
	0.25	0.62		0.50	0.14
				0.25	0.12
40	0.50	1.20	30	0.50	0.16
	0.25	1.35		0.25	0.15
			40	1.00	0.38
				0.50	0.40
				0.25	0.35
$\Delta H^{\neq} = 13.5$ kcal/mole, $\Delta S^{\neq} = -13.2$ e.u.			$\Delta H^{\neq} = 11.9$ kcal/mole, $\Delta S^{\neq} = -23.9$ e.u.		

(change of k_2 at two temperatures for C_6F_5HgBr and three temperatures for C_6Cl_5HgBr) are also shown in Table 2.

Iododemercuration in DMSO

Iododemercuation of (pentafluorophenyl)mercury bromide in DMSO was studied at equimolar reagent concentrations $(0.5\text{–}1) \times 10^{-3}$ mole/l at temperatures 19, 30, 40°. The reaction obeys the first order kinetics (Table 3). Anamorphoses of kinetic curves are shown in Fig. 7.

Temperature dependence of the log $k_1 = f(1/T)$ of reaction rate constant is presented in Fig. 8. $\Delta H^{\neq} = 13.3 \pm 0.3$ kcal/mole, $\Delta S^{\neq} = -38.2$ e.u.

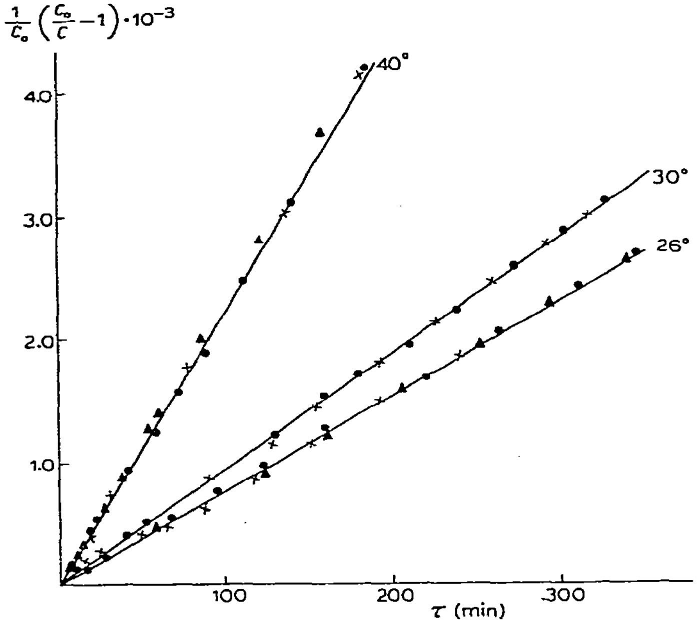


Fig. 6. Dependence $1/C_0(C_0/C-1)=f(\tau)$ for reaction of C_6Cl_5HgBr with I_3^- in DMF at various temperatures (× $C_0=0.25\times10^{-3}$ mole/l, ● $C_0=0.5\times10^{-3}$ mole/l, ▲ $C_0=1\times10^{-3}$ mole/l).

TABLE 3

$C_6F_5HgBr+I_2$, DMSO

Temp. (°C)	$C_0\times10^3$ (mole·l^{-1})	$k_1\times10^5$ (sec^{-1})
19	1	2.3
30	1	5.6
	0.5	5.5
40	1	11.1
	0.5	10.2

Iododemercuration in benzene

Without nucleophilic catalysts C_6F_5HgBr and C_6Cl_5HgBr do not react with iodine in benzene. Optical density of the solutions at 20° does not change for many hours. A vigorous reaction occurs on adding iodide ions giving iodobenzenes in quantitative yields. Analogous to reaction in DMF the optical density of the solution sharply falls upon mixing the solutions of I_3^- and organomercury compound [at $C_0=0.5\times10^{-4}$ mole/l, 21° and $\lambda=390$ nm, $D_0=0.800$, and in case of C_6F_5HgBr D_0 (reaction mixture) $=0.389$]. Iododemercuration of C_6Cl_5HgBr was conducted at concentrations $(0.25–0.5)\times10^{-3}$ mole/l, whereas considerably lower concentrations, $(1–0.25)\times10^{-4}$ mole/l, were used in the very fast reaction with C_6F_5HgBr. Both reactions are described by the second order kinetics. Anamorphoses of kinetic curves $D_0/D-1=f(t)$ at 21.5° are shown in Figs. 9 and 10. The values of constants k_2 show rather good agreement at different starting concentrations (Table 4).

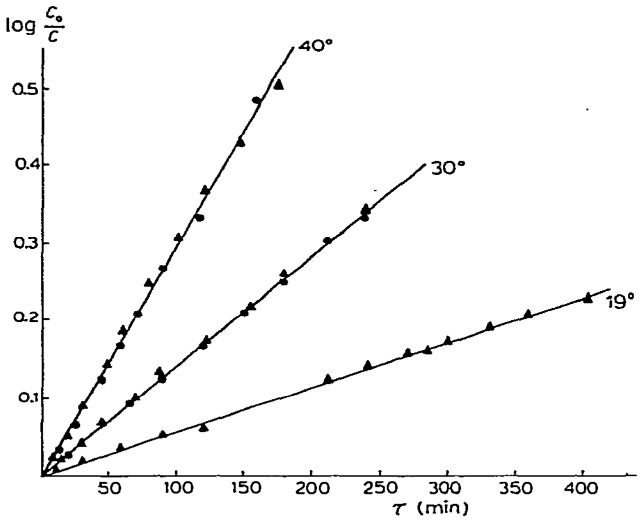


Fig. 7. Dependence log $C_0/C = f(\tau)$ for reaction of C_6F_5HgBr with I_2 in DMSO at various temperatures (● $C_0 = 0.5 \times 10^{-3}$ mole/l, ▲ $C_0 = 1 \times 10^{-3}$ mole/l).

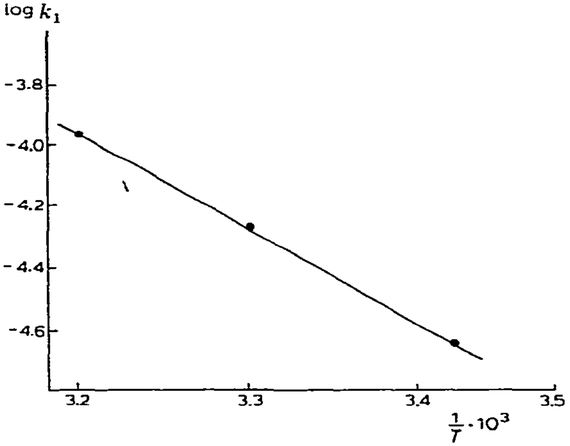
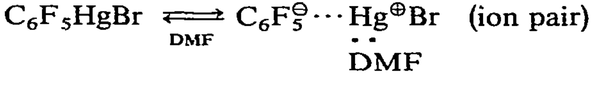


Fig. 8. Dependence log $k_1 = f(1/T)$ for reaction of C_6F_5HgBr with I_2 in DMSO.

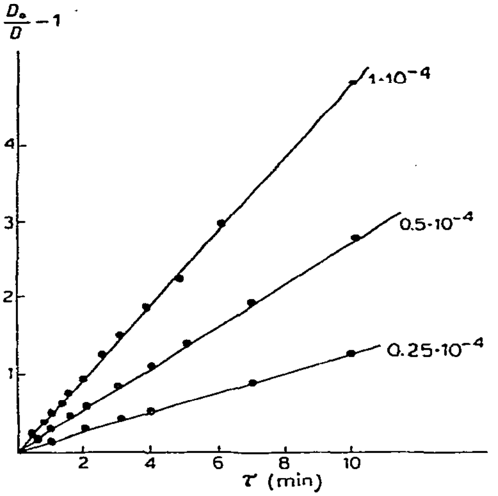
DISCUSSION

In accordance with the earlier presentations[2] in the first reaction step which determines the rate of entire process involves ionization of organomercury compound under the action of DMF. The fast step being the reaction of generated ion pair with iodine [S_E1(DMF) mechanism].



$$C_6F_5HgBr \underset{DMF}{\overset{slow}{\rightleftharpoons}} C_6F_5^{\ominus} \cdots \underset{\underset{DMF}{\cdot\,\cdot}}{Hg^{\oplus}}Br \quad \text{(ion pair)}$$

$$\text{Ion pair} + I_2 \xrightarrow{fast} C_6F_5I + HgBrI$$



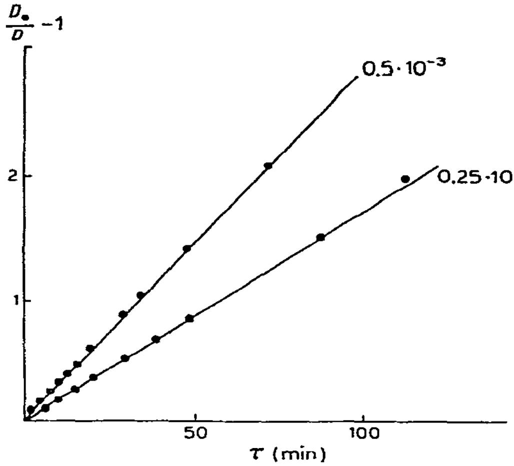


Fig. 9. Dependence $D_0/D - 1 = f(\tau)$ for reaction of C_6F_5HgBr with I_3^- in benzene at various concentrations.

Fig. 10. Dependence $D_0/D - 1 = f(\tau)$ for reaction of C_6Cl_5HgBr with I_3^- in benzene at various concentrations.

TABLE 4

$C_6F_5HgBr + I_3^-$, C_6H_6, 21.5°		$C_6Cl_5HgBr + I_3^-$, C_6H_6, 21.5°	
$C_0 \times 10^4$ (mole·l⁻¹)	k_2 (l·mole⁻¹·sec⁻¹)	$C_0 \times 10^3$ (mole·l⁻¹)	k_2 (l·mole⁻¹·sec⁻¹)
1	80	0.5	0.94
0.5	85.6	0.25	1.03
0.25	85.6		

RHgX and iodine (or I_3^-) give rise to an inorganic mercury salt (or complex HgX_3^-) which should change both the optical density of iodine (or I_3^-) solutions and also the reactivity of iodinating agent (this was actually shown in the closed experiments). Thus it could be expected that the value of reaction rate constant would not remain constant in the course of kinetic curve; nevertheless it can be seen that it remains the same within the whole range of kinetic curve. This is a common feature for iododemercuration reactions of asymmetric organomercury compounds, RHgX, as well, the kinetics of which has been studied by spectrophotometric method (for example, reactions of ArHgX with I_2 in DMF[13] and Py[14]). In these reactions the inorganic mercury formed salt did not affect the magnitude of the constant estimated from an optical density change of iodine solution.

The kinetics of reaction between C_6F_5HgBr and iodine in DMF was investigated by accumulation of the reaction product pentafluoroiodobenzene with GLC. The reaction rate constant was calculated from the equation:

$$k_1 = \frac{2.303}{\tau} \log \frac{C_\infty}{C_\infty - C_\tau}$$

where C_∞ is the final concentration of C_6F_5I, C_x is the product concentration at the moment of time τ, which can be calculated from the formula:

$$\frac{S_{st}}{S_x} = k \cdot \frac{M_{st}}{M_x} \cdot \frac{C_{st}}{C_x}$$

where S_{st} is the peak area of the standard, S_x is the C_6F_5I peak area; M_{st}, M_x are mol. wt. of the standard and C_6F_5I, respectively. C_{st} is the concentration of the standard and k is the calibration coefficient.

Investigation was conducted at the reagent concentrations (1×10^{-2} mole/l) ten times exceeding those employed in spectrophotometric measurements. In parallel with the GLC analysis the spectroscopic measurements were carried out at the same concentration. The values k_1 obtained are in a good agreement: $k_1^{30} = 1.29 \times 10^{-4}$ sec^{-1} (spectrophotometric method), $k_1^{30} = 1.18 \times 10^{-4}$ sec^{-1} (GLC method). (The values somewhat differ from those obtained in the spectrophotometric investigations, because other DMF portion was used.)

The first order reaction rate constant calculated from the amount of accumulated reaction product is also in good consistency in the entire range of kinetic curve. Thus the forming inorganic mercury salt does not affect the magnitude of the reaction rate constant although the reason is not known yet.

The reaction mechanism proposed does not take into account possible equilibrium in solution:

$$\text{RHgX} + I_2 \overset{K_{eq}}{\rightleftharpoons} \text{RHgX} \cdot I_2$$

The first order observed makes one to assume that only the "free" organomercury molecules may undergo ionization and the observed reaction rate constant is an effective one. Taking in account a large difference in the carbanion stabilities for $C_6F_5^\ominus$ and $C_6Cl_5^\ominus$ (the pK_a's of the respective CH-acids are 23 and 30.5[15]), it should be expected that the reactivities of the organomercury compounds under study would differ essentially under conditions of the $S_E1(N)$ mechanism[16]. Even in terms of an ionization (instead of dissociative) mechanism, the reactivity of C_6F_5HgBr should exceed that of C_6Cl_5HgBr, since the more "acidic" radical makes easier the coordination of a solvent molecule with mercury and thus facilitates the C–Hg bond ionization. However the observed rate reduction in going from C_6F_5HgBr to C_6Cl_5HgBr (although it agrees with the S_E1 representations) is rather small, and it is entirely associated with a sharp drop in an activation entropy which was partially leveled by a decrease in activation enthalpy (both of these facts can not be trivially interpretated).

An unexpected result [hard to explain in terms of the $S_E1(N)$ mechanism] was obtained in DMSO, in which iododemercuration of C_6F_5HgBr was somewhat slower as compared with that in DMF.

It is interesting that analogous to a replacement of radical (C_6F_5 by C_6Cl_5) a decrease in the activation entropy is responsible for such decrease in the rate, which indicates that the structure of transition state in DMSO is more complex.

In the presence of iodide ion both compounds react much faster by the second order kinetics.

Earlier it has been found[17] that asymmetric organomercury compounds, RHgX ($R \neq Ar$), react with iodine in DMF according to a radical mechanism. In the presence of iodide ion the reaction mechanism alters to electrophilic bimolecular substitution.

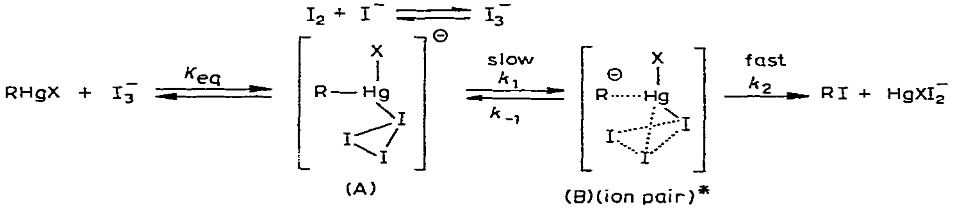
From the data discussed it follows that the electron-attractive substituents in organomercury compounds influence essentially their behaviour in the iododemercuration reaction. It is probably that a nucleophilic solvent, DMF, acts as a nucleophilic catalyst, thus the reaction follows the S_E1(DMF) mechanism, analogous to S_E1(DMSO) reaction of the mercury isotopic exchange between C_6F_5HgBr and $HgBr_2$ labeled by ^{203}Hg (ref. 18). It might be expected that in the presence of iodide ion the anions I^- or I_3^- would play the role of a nucleophilic catalyst.

The second order observed in these reactions agrees with the idea that a reagent molecule I_3^- acts as a nucleophilic catalyst[2]. Strong interaction between RHgX and I_3^- specifically in case of C_6F_5HgBr is evident from a sharp change in optical density of iodine solutions (I_3^-) upon addition of organomercury compound. Iododemercuration by I_3^- in DMF at 30° proceeds four times faster for perfluorinated organomercury compound with respect to perchlorinated derivatives, *i.e.* under conditions described the reactivity changes of these compounds are relatively small.

From a comparison of thermodynamic parameters it can be seen that the rate decrease, as in the case of reaction with I_2, is due to a decreasing activation entropy which is again partially leveled by a lower enthalpy of activation.

Thus we assume that in reaction of RHgX ($R=C_6F_5$, C_6Cl_5) with I_3^- the observed kinetic dependences are associated with the nucleophilic catalysis by the second reagent rather than with the change of mechanism (from S_E1 to S_E2).

That the Lambert–Beer law is held when the initial concentration of reagents is varied and the observed rate constant remains unchanged are not in contradiction with the assumption that the organomercury compound is completely complexed by I_3^-. However, this assumption need a special examination. The reaction mechanism may include ionization of C–Hg bond in the complex $RHgX \cdot I_3^-$ as the slowest step, and an intramolecular reaction in the ion pair leading to the C–I bond formation as the fast step.



(* here the term ion pair is conditional because we do not have oppositely charged components).

When the stationary principle is fulfilled

$$W = \frac{k_1 \cdot k_2}{k_{-1} + k_2} \cdot (\mathrm{RHgX}) \cdot (\mathrm{I_3^-}),$$

if $k_{-1} \ll k_2$ then $W = k_1 \cdot (\mathrm{RHgX}) \cdot (\mathrm{I_3^-})$, where the C–Hg bond ionization to the ion pair (B) is the limiting step. This example is kinetically indistinguishable from the mechanism for which $k_{-1} \gg k_2$ (the ion pair regeneration proceeds faster than its "closure" resulting in the C–I bond formation).

$$W = K \cdot k_2 \cdot (\text{RHgX}) \cdot (I_3^-) \quad \text{where} \quad K = \frac{k_1}{k_{-1}}$$

In such case electrophilic attack at the carbon atom is the limiting step. This mechanism differs from that of the regular bimolecular electrophilic substitution S_Ei only by a necessity of a pre-equilibrium ionization step of organomercury compound. Different reactivities of C_6F_5HgBr and C_6Cl_5HgBr in such mechanism are explained by the different K's. But a community of the dependences observed with iododemercuration by iodine makes it possible to assume that the first mechanism is more probable.

For both compounds the reaction rate with I_3^- increases considerably in going from DMF to benzene. The largest ($\sim$2 order) change in the rate is observed for C_6F_5-HgBr. Besides, as seen from the data of Table 4, the difference in reactivities of these compounds becomes more essential. Apparently this is due to a higher activity of iodide ion and to the stronger complexation of RHgX with I_3^- in a nonpolar solvent, which unlike DMF does not hinder the reaction. In such a case the observed rate differences are more accurate to make comparison with the different reactivities of compounds towards complexation and coordination of anions. Taking into account the fact that halogen substituted phenylmercury bromides do not react with iodine in benzene and that the electrophilic nature of iodinating agent decreases from I_2 to I_3^-, the faster reaction rate (as compared to that in DMF) may be explained on the basis of nucleophilic catalysis (nucleophilic coordination). Again in the case of DMF, we assume [although it indicates $S_E1(N)$ reaction course in benzene] that the C–Hg bond ionization in the complex A is the limiting step of the process rather than the electrophilic attack of iodine at the mercury atom.

Much higher reactivity of C_6F_5HgBr against C_6Cl_5HgBr is also in agreement with a possible realization of the $S_E1(I_3^-)$ mechanism[2].

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