STUDY OF IODODEMERCURATION OF SYMMETRICAL ORGANOMERCURY COMPOUNDS

I. P. BELETSKAYA, L. V. SAVINYKH and O. A. REUTOV

Department of Chemistry, Moscow State University, Moscow (U.S.S.R.)

(Received July 27th, 1970)

SUMMARY

Iododemercuration of symmetrical organomercury compounds, R_2Hg, was investigated in a number of solvents (CCl_4, dioxane, DMF, HMPA). The relative reactivity of the compounds was obtained in these solvents. It was shown that the $S_E i$ reaction rate could not serve as a measure of the nucleophilic nature of the organic group.

High reaction rates with I_2 in the aprotic dipolar media were obtained for the compounds containing strong electron-attractive substituents. In such cases the reactions are assumed to follow the $S_E 1(N)$ mechanism.

INTRODUCTION

Some attempts has been reported to derive a series of relative reactivity of organic groups on the basis of comparison of the rates of proto- and halodemetallation reactions of various derivatives with just the same metal R–M. Different rates of reactions between R–M and electrophile E–N have been assumed to depend upon tendencies of organic group R to undergo electrophilic attack. However it can be easily shown (which is evident from the great number of inconsistent results[1]) that it is not possible to obtain the series for the change of the nucleophilic nature of R by comparing the reaction rates. This is due to the fact that organometallic reactions often proceed by the $S_E i$ mechanism (especially with unsymmetrical organometallic compounds $R_{n-m}MX_m$) in which a nucleophilic coordination with the metal atom is essential[1].

$$\begin{bmatrix} R{-}m \\ \vdots \quad \uparrow \\ E{-}N \end{bmatrix}^{\neq}$$
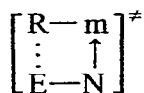
Not only the nature of the metal atom but also the organic group R has an influence on such coordination. Besides, in solvating media the ability of organometallic compounds to undergo solvation also depends upon the nature of the group R. And naturally the expected "radical reactivity" series depends on the nature of electrophilic agent. Finally, possible change of mechanism from $S_E i$ to $S_E 1(N)$[2] for sufficiently electron-attracting groups has not been considered.

In the present work we studied the effect of different groups R on the rate of iododemercuration reaction in a series of symmetrical organomercury compounds, R_2Hg. Solvents of different polarities and specific solvating abilities towards the reagents were used *e.g.* carbon tetrachloride, dioxane, dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPA).

We investigated symmetrical compounds because under conditions of bimolecular electrophilic substitution these are more reactive than the corresponding unsymmetrical derivatives. Also with equimolar ratio of reagents the reaction stops at the first step[*,3]:

$$R_2Hg + I_2 \rightarrow RHgI + RI$$
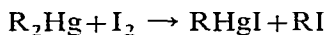
Furthermore as it follows from the data on complexation[5] the role of solvation and nucleophilic coordination for these compounds is essentially with respect to unsymmetrical RHgX derivatives. From the study of substituent effects [for example in the set[6] $(XC_6H_4)_2Hg$] an electrophilic iodine attack at the carbon atom is known to determine the reaction rate, although the I→Hg coordination can smooth the effect of the organic group nature to a certain extent[7].

We investigated some symmetrical organomercury compounds in which mercury was bonded to a saturated, olefinic or aromatic carbon atom. The compounds with strong electron-attracting groups have also been studied.

EXPERIMENTAL

Kinetic investigation of iododemercuration reaction was conducted by spectrophotometric method using a CF-4 instrument and thermostatted cuvettes by measuring the change in iodine optical density at λ 520 nm in CCl_4, 450 nm in dioxane and 430 nm in DMF and HMPA. The equimolar reagent concentrations varied within $(0.25–1.00) \times 10^{-3}$ mole/l.

The organomercury compounds were prepared according to reported methods[8,9]. CCl_4, dioxane and DMF were purified according to known methods[10,11]. Schuchardt HMPA was purified from amines by the known procedure[11] and distilled twice over CaH_2 under an argon stream and stored over molecular sieves (4A and 3A). Since the rate of iododemercuration reaction varies upon storage of such solvents as dioxane and DMF (although the regularities observed completely preserve), all investigations were conducted with the same portion of freshly purified solvent. All the data were found to be reproducible.

Quantitative yield of pentafluoroiodobenzene in iododemercuration of $(C_6F_5)_2Hg$ in DMF was confirmed by preparative isolation. For reaction of [C-$(CF_3)_2COOEt]_2Hg$ with I_2 the reaction products were analyzed on a Chrom-2 chromatograph with flame ionization detector, column length 2 m, $\varnothing$ 4 mm, 17% apiezon L on chromosorb W. Carrier gas: nitrogen, rate 90 ml/min, internal standard *p*-xylene, column temp. 90°. Yield of $IC(CF_3)_2COOEt$ 96.7%.

Quantitative yield of $(CF_3)_3CI$ was confirmed with the ^{19}F NMR method (on JNM-4H-100 instrument) by comparison with an authentic sample.

---

* Earlier it has been found that unsymmetrical RHgX (R≠Ar) compounds react with iodine by a radical mechanism[4].

RESULTS AND DISCUSSION

Reaction in carbon tetrachloride

Reaction in CCl_4 is the most suitable case for investigating the effect of the radical nucleophilicity of the reaction rate of symmetrical organomercury compounds with iodine. This reaction has been studied earlier by Razuvaev and Savitskii[3] who obtained the parameters of Arrhenius equation for the set R_2Hg. Using their values we estimated the second order reaction rate constants. The results obtained are in good agreement with our data. We note that the data of ref. 3 do not provide a linear dependence between E and log A, *e.g.* the reaction set discussed is not isokinetic. In CCl_4 the reaction is of the second order, the constants are listed in Table 1.

TABLE 1

$R_2Hg + I_2$, CCl_4, 19.8°.

R in R_2Hg	$C_0 \times 10^3$ (mole·l^{-1})	k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$)	k_2 (19.8°) ($l \cdot mole^{-1} \cdot sec^{-1}$)[a]
C_6H_5	1	3.87	3.20
	0.5	3.27	
$C_6H_5CH_2$	1	3.40	3.00
	0.5	3.33	
$CH_2=CH$	1	1.17	
C_2H_5	1	0.39 (18°)	0.44
$n-C_3H_7$	1	0.46	
$n-C_4H_9$	1	0.37	0.38
CH_3	1	0.001	0.001, 0.0012 (28°)[b]
$CH=CHCl$	1	0.11	
	1	0.48 (40°)	
CH_3OOC	1	1.16×10^{-2}	
	1	1.4×10^{-1} (40°)	
C_6F_5	1	4.5×10^{-3}	
	0.25	5.3×10^{-3}	
	1	3.0×10^{-2} (40°)	
$CH(CF_3)COOEt$	1	c	
$C(CF_3)_2COOEt$	1	d	
$C(CF_3)_3$	1	d	
CH_3COCH_2	0.25–1	e	

[a] Ref. 3. [b] Ref. 18. [c] Optical density did not change during 2 days. [d] No reaction. [e] Instantaneously.

It can be seen from the data of Table 1 that the reaction rate depends considerably on the nature of organic group, and in going from diphenylmercury, for example, to its perfluorinated analogue it decreases 500-fold. It is known that phenyl and vinyl metal derivatives are most active in the S_E2 reactions. Such behaviour may be due to a transition state close to the σ-complex for Ar_2Hg and generally owing to the participation of π-electron system in the transition state stabilization.

Except for dimethylmercury, the reaction rates of dialkylmercury derivatives are fairly close to each other. Probably there is an overlapping of the polar and steric effects. An abnormally low reaction rate, of dimethylmercury is absolutely incomprehensible. Earlier Dessy and Zee[12] also observed an analogous behaviour in the

reaction of R_2Hg with HgX_2 in dioxane and the results are somewhat inconsistent with those of the British authors[13] where the reactivity of Me_2Hg in the system R_2Hg/HgX_2/ethanol exceeded that of Et_2Hg. The reaction rates of dibenzyl- and bis(2-chlorovinyl)mercury are abnormally fast.

It is important to note that bis(pentafluorophenyl)mercury is capable unlike unsymmetrical C_6F_5HgBr[14] to react with iodine in CCl_4. The reaction proceeds by an electrophilic mechanism though it is rather slow. This is another evidence of the higher nucleophilic character of symmetrical organomercury compounds, R_2Hg, with respect to unsymmetrical, $RHgX$, R being the same. Under conditions employed the compounds with strong electron-attracting groups, $[CH(CF_3)COOEt]_2Hg$, $[C(CF_3)_2COOEt]_2Hg$ and $[C(CF_3)_3]_2Hg$, undergo practically no reaction.

Reaction in dioxane

In going from CCl_4 to dioxane the reaction rate of diphenyl- and dialkylmercury derivatives increases somewhat, which is significant (about 20-fold at 20°) for divinylmercury. But the reaction is slower (5–10 times at 40°) with compounds containing electron-attracting groups R (R = Cl–CH=CH, $COOCH_3$, C_6F_5). However, the relative reactivities do not change much, except that of divinyl mercury which was found to be very reactive in dioxane. (Table 2).

In going from such non-solvating solvents as CCl_4 to dioxane the observed rate increase is associated with the solvation of organomercury compound thus

TABLE 2

$R_2Hg + I_2$, DIOXANE

R in R_2Hg	$C_0 \times 10^3$ (mole·l^{-1})	k_2 (l·mole^{-1}·sec^{-1}) at		
		20°	30°	60°
CH_2=CH	1	19.0		
	0.5	20.7		
C_6H_5	1	5.55		
	0.5	5.44	9.0	
	0.25		10.3	45.6
$C_6H_5CH_2$	1	2.50		
	0.5	2.50	5.78	14.3
	0.25		5.78	14.5
C_2H_5	1	1.71		
	0.5	1.71	3.34	20.0
	0.25		3.55	22.4
n-C_3H_7	1	1.79		
	0.5	1.83	3.08	18.8
	0.25			18.6
n-C_4H_9	1	1.50		10.7
	0.5	1.47	2.54	11.1
CH=CH–Cl	1	1.19×10^{-2}	3.31×10^{-2} (40°)	7.78×10^{-2}
CH_3OOC	1	2.11×10^{-2} (30°)	2.97×10^{-2} (40°)	
C_6F_5	1	1.60×10^{-3}	4.1×10^{-3} (40°)	1.02×10^{-2}
CH_3	1			1.41×10^{-1}
	0.5			1.40×10^{-1}

enhancing the nucleophilic character of the substrate. The compounds in which R is an electron-attracting group are most solvated. Thus one should expect a faster reaction. But actually the effect is quite opposite. Probably such behaviour is a result of iodine solvation by dioxane which increases its electrophilic character. Apparently the compounds with strong electron attracting groups for which in general the electrophilic reactions without nucleophilic catalysts are rather difficult to occur were found to be most sensitive towards decreasing electrophilic properties of the agent. The complexation effect $I_2 \cdot$ dioxane on the reaction rates is dominating over increasing nucleophilic property of R_2Hg on account of coordination with the solvent.

The temperature dependence for the rate of iododemercuration reaction was investigated in dioxane. Thermodynamic parameters are listed in Table 3. High iododemercuration rate of divinylmercury prevented to investigate its temperature dependence.

TABLE 3

R in R_2Hg	ΔH^* (kcal/mole)	$-\Delta S^*$ (e.u.)
C_6H_5	9.0	22.3
$C_6H_5CH_2$	14.0	5.7
C_2H_5	11.2	17.1
$n-C_3H_7$	9.6	22.4
$n-C_4H_9$	8.6	26.2
$CH=CH-Cl$	8.9	34.9
CH_3OOC	5.7	45.3
C_6F_5	8.4	40.6

It is significant that exclusively a decrease in activation entropy is responsible for the sharp rate decrease for R_2Hg with electron-attracting groups. Probably it is due to unfavourable steric factors arising in the transition state of two strongly solvated reagents.
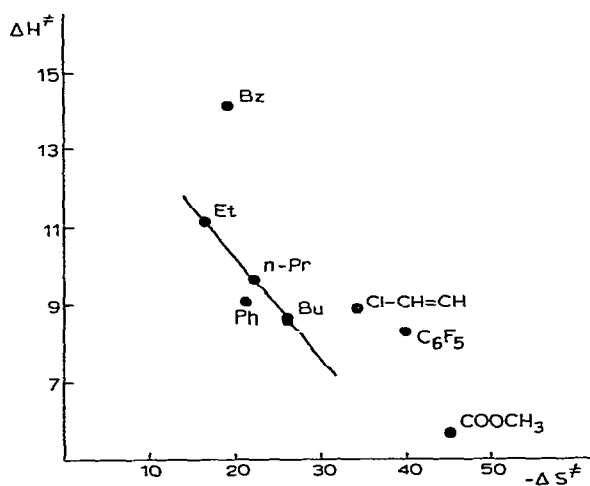

Fig. 1. Dependence ΔH^* and ΔS^* for iododemercuration of R_2Hg in dioxane.

TABLE 4

$R_2Hg + I_2$, DMF

R in R_2Hg	$C_0 \times 10^3$ (mole·l^{-1})	k_2 (l·mole^{-1}·sec^{-1}) at	
		10°	40°
$CH_2=CH$	1	24.7	
	0.5	25.8	
	0.25	25.9	
C_6H_5[a]	1	20.1	
	0.5	20.0	
	0.25	20.6	
C_2H_5	1	10.65	
	0.5	10.40	
	0.25	10.50	
n-C_3H_7	1	6.72	
	0.5	6.90	
	0.25	6.60	
n-C_4H_9	1	5.42	
	0.5	5.90	
	0.25	5.80	
i-C_3H_7[b]	1	4.70	
	0.5	3.82	
	0.25	3.68	
$C_6H_5CH_2$	1	3.33	
	0.5	3.51	
	0.25	3.46	
$CH=CH-Cl$[c]	1	5.41	28.0
	0.5	5.52	
	0.25	5.45	
CH_3OOC[c]	1	1.56×10^{-2}	9.33×10^{-2}
	0.5	[d]	
	0.25		
C_6F_5[c]	1		2.40×10^{-2}
$CH(CF_3)COOEt$[c]	1		3.38×10^{-4}
	0.5		3.39×10^{-4}
	0.25		3.30×10^{-4}
$C(CF_3)_2COOEt$	1.05–0.125	[f]	
$C(CF_3)_3$	1.00–0.062	[f]	
CH_3COCH_2	1.00–0.25	[f]	

[a] Apparently due to the different purification procedures used for DMF the k_2 is different from that obtained earlier[6]. [b] The rate constant varience is probably due to an oxidation of (i-Pr)$_2$Hg (see refs. 15 and 16). [c] The k_2's are calculated from the starting rates. The constant increases somewhat in the course of the kinetic curve. [d] The reaction rate increases upon dilution. [e] The k's are given in sec^{-1}. [f] Instantaneously.

There is no linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for iododemercuration of symmetrical organomercury compounds in dioxane (Fig. 1) although the points corresponding to the alkyl substitutents are in the same line. This serves as a proof that a transition state structure substantially changes in going from Alk$_2$Hg to Ph$_2$Hg and R_2Hg with R = electron-attracting groups.

Reaction in DMF

When DMF was used instead of dioxane the reaction rates increased essentially

for all organomercury compounds (Table 4).

Undoubtfully DMF increases the reaction rate owing to the high dielectric constant of the medium and to increasing nucleophilicity of R_2Hg due to its coordination with the solvent. For all the compounds simultaneous effect of all these factors is probably more essential than a decreasing electrophilic nature of the agent in the complex $I_2 \cdot DMF$.

The general order of the effect of group R was almost unchanged although for alkyl derivatives there is a distinct decrease in the series Et > n-Pr > n-Bu > i-Pr in reactivity. Apparently this is a result of the greater role of steric factor in a strongly solvating solvent. Significant break in the order is resulted in case of the 2β-chlorovinyl group due to an abnormally high reaction rate of bis(2-chlorovinyl)mercury in DMF. In view of that the reaction rates of other compounds with electron-attracting groups $Hg(COOCH_3)_2$ and $Hg(C_6F_5)_2$ do not undergo such a sharp change and the above behaviour for other compounds is incomprehensible. Thus the following sequence on the rate of iododemercuration of R_2Hg is observed:

CCl_4: Ph > PhCH$_2$ > CH$_2$=CH > Alk > ClCH=CH > CH$_3$OOC ~ CH$_3$ > C$_6$F$_5$

Dioxane: CH$_2$=CH > Ph > PhCH$_2$ > Alk > ClCH=CH > CH$_3$OOC ~ CH$_3$ > C$_6$F$_5$

DMF: CH$_2$=CH > Ph > Et > n-Pr > n-Bu ~ ClCH=CH > i-Pr ~ PhCH$_2$ >
    CH$_3$OOC > C$_6$F$_5$

Although the order of groups in the series in various solvents does not change, however there is no linear dependence between the logs of rate constants for any pair of solvents. Invalidity of the nonlinearity principle for the change of free energy on changing the solvent, on the other hand the absence of compensating effect at the change of radical are another evidence that the reaction rates of organomercury compounds with electrophilic agents can not serve as a criterion for estimating the nucleophilic character of the metal bonded organic group.

It is most interesting that at 10° (in the concentration range from 6.2×10^{-5} to 1×10^{-3} mole/l) iododemercuration reactions of $[(CF_3)_3C]_2Hg$ and $[C(CF_3)_2-COOEt]_2Hg$ (which were inert in CCl_4 and dioxane) proceed almost instantaneously in DMF. Unsymmetrical organomercury compounds also undergo instantaneous reaction under these conditions. These compounds contain the most electron-attracting radicals, acidities of the respective CH-acids in DMF are 7 and 13 (ref. 17). We assume that such sharp change in reactivities of these compounds is owing to the $S_E1(N)$ reaction with iodine in DMF[2]. This is confirmed by the fact that the reaction of $[(CF_3)CHCOOEt]_2Hg$ (pK_a $CF_3CH_2COOEt = 15$) is of the first order, the constant k_1 being uneffected with a change in starting reagent concentrations from 0.25×10^{-3} to 1×10^{-3} mole/l.

Reaction rate of diacetonylmercury was abnormally high. Analogous behaviour was observed by us for protodemercuration reaction and reaction with iodine in CCl_4. The compounds with electron-attracting groups are characterized by some increase in the rate constant in the course of kinetic curve, which is explained by a possibility of $S_E1(N)$ concurrent iododemercuration of formed unsymmetrical compound, which may react faster than the symmetrical derivatives. For example, the reaction of C_6F_5HgBr with I_2 in DMF is of the first order[14], $\tau_{\frac{1}{2}} = 150$ min at 30°, i.e. under the same conditions its rate far exceeds that of iododemercuration of $(C_6F_5)_2Hg$.

Such phenomenon always takes place when both compounds R_2Hg and RHgX react in accord with $S_E1(N)$ mechanism which is due to the fact that unlike the $S_E i$ and $S_E 2$ reactions, under conditons of this mechanism RHgX is more reactive than R_2Hg.

Investigating the reactions of R_2Hg containing the electron-attracting groups we observed incomprehensible behaviour demanding special study: in a number of cases we observed that the reaction rate increases with decreasing reagent concentrations. For example the reaction of $Hg(CH_3OOC)_2$ with I_2 in DMF at $40°$ is faster even when concentration is two times lower. This also occurred in CCl_4. As we have mentioned above optical density of iodine solution in the system $[CH(CF_3)COOEt]_2$-$Hg/I_2/CCl_4$ at 40 and $C_0 = 1 \times 10^{-3}$ mole/l did not change even after two days, however at concentration 0.25×10^{-3} mole/l it decreased very slowly although making invalid the kinetic equations of integer orders.

Reaction in HMPA

Unexpected result was obtained for iododemercuration reaction in a strong aprotic dipolar solvent as HMPA. Compared with DMF occurred a sharp decrease in the rates of reactions which followed the $S_E 2$ mechanism (Table 5). Apparently an essentially lower electrophilic character of iodine due to complexation with HMPA is responsible for such an effect.

TABLE 5

$R_2Hg + I_2$, HMPA

R in R_2Hg	$C_0 \times 10^3$	k_2 (l·mole^{-1}·sec^{-1}) at	
	(mole·l^{-1})	$20°$	$60°$
C_6H_5	1	0.41	
	0.5	0.41	
	0.25	0.43	
$C_6H_5CH_2$	1		0.21
	0.5		0.21
CH=CH–Cl	1	0.14	
	0.5	0.13	
	0.25	0.17	
$C_6F_5{}^a$	0.5		0.27
	0.25		0.29
$C(CF_3)_2COOEt$	1–0.25	^{b}	
$C(CF_3)_3$	1–0.25	^{b}	

^{a} k_2 increases up to 0.8 in the course of kinetic curve. ^{b} Instantaneously.

The compounds with strong electron-attracting groups are an exception. The rate of reaction of $(C_6F_5)_2Hg$ with I_2 does not decrease in changing the solvent from DMF to HMPA; whereas the most "acidic" compounds $[C(CF_3)_2COOEt]_2Hg$ and $[C(CF_3)_3]_2Hg$ react instantaneously. Probably in the latter solvent the effect of complexation $R_2Hg \cdot HMPA$ (for $R = C_6F_5$) exceeds an effect of decrease in the electrophilic nature of iodine while for $R = C(CF_3)_2COOEt$ and $C(CF_3)_3$ the reaction mechanism changes from $S_E 2$ to $S_E 1(N)$.

REFERENCES

1 I. P. BELETSKAYA, *Dokl. Akad. Nauk SSSR*, 184 (1969) 1331.
2 I. P. BELETSKAYA, K. P. BUTIN AND O. A. REUTOV, *Organometal. Chem. Rev.*, in press.
3 G. A. RAZUVAEV AND A. V. SAVITSKII, *Dokl. Akad. Nauk SSSR*, 85 (1952) 575.
4 I. P. BELETSKAYA, T. P. GUR'YANOVA AND O. A. REUTOV, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1961) 2178.
5 O. A. REUTOV AND I. P. BELETSKAYA, *Reaction Mechanisms of Organometallic compounds*, North-Holland Publ. Comp., Amsterdam, 1968, ch. 6.
6 I. P. BELETSKAYA, A. L. KURTS, N. K. GENKINA AND O. A. REUTOV, *Zh. Org. Khim.*, 4 (1968) 1120.
7 A. L. KURTS, I. P. BELETSKAYA AND O. A. REUTOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 2207.
8 L. G. MAKAROVA AND A. N. NESMEYANOV, *Metody Elementoorganicheskoi Khimii.* Rtut', "Nauka" Publ. House, Moscow, 1965, pp. 25, 27, 29, 45, 255.
9 I. L. KNUNYANTS, B. R. POLISHCHUK AND L. S. GERMAN, *Avtorskoe svidetel'stvo No. 256771, Bull. Izobretenii*, 35 (1969) 27.
10 C. A. KRAUS AND R. A. VINGEL, *J. Amer. Chem. Soc.*, 56 (1934) 511.
11 AUTORENKOLLEKTIV DER TECHNISCHEN UNIVERSITÄT DRESDEN, *Organisch-Chemisches Grundpraktikum*, 3. Aufl., VEB Deutscher Verlag der Wissenschaften, Berlin, 1964.
12 R. E. DESSY AND I. K. LEE, *J. Amer. Chem. Soc.*, 82 (1960) 689.
13 E. D. HUGHES AND H. C. VOLGER, *J. Chem. Soc.*, (1961) 2359.
14 I. P. BELETSKAYA, L. V. SAVINYKH, V. N. GULYACHKINA AND O. A. REUTOV, *J. Organometal. Chem.*, 26 (1971) 23.
15 M. M. KREEVOY AND R. Z. HANSEN, *J. Phys. Chem.*, 65 (1961) 1055.
16 YU. A. ALEKSANDROV, O. N. DRUZHKOV, C. F. ZHIL'TSOV AND G. A. RAZUVAEV, *Dokl. Akad. Nauk SSSR*, 157 (1964) 1395.
17 K. P. BUTIN, A. N. KASHIN, I. P. BELETSKAYA, L. S. GERMAN AND V. R. POLISHCHUK, *J. Organometal. Chem.*, 25 (1970) 11.
18 A. LORD AND H. O. PRITCHARD, *J. Phys. Chem.*, 70 (1966) 1689.