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# KINETICS OF THE REACTIONS OF DIARYLIODONIUM

## SALTS WITH MERCURY

т.	L.	Kim, O. A. Ptitsyna,	UDC 541.127:542.91:547.539.4:546.49
К.	Р.	Butin, and O. A. Reutov	

Together with the Mg-organic syntheses, the reactions of the onium (diazonium, oxonium, halonium, etc.) salts with metals are among the basic methods followed in preparing the aryl organometallic compounds. Typical instances are found in the reactions of diaryliodonium salts (DAS) with metallic mercury [1-3], processes leading to the formation of organomercury compounds in high yield

$$Ar_2IX + Hg \rightarrow ArI + ArHgX$$
 (1)

A mechanism involving one-electron reduction of the DAS by metallic mercury with the formation of an  $Ar_2I$ . radical which breaks down homolytically to ArI and an Ar  $\cdot$  radical, the latter recombining with an XHg  $\cdot$  radical to form the ArHgX compound, has been proposed for these reactions [2, 3]:

Although such a mechanism is entirely consistent with the experimental data on type (1) reactions, alternative mechanisms, e.g., a penetration mechanism similar to that described for the reactions of metallic mercury with Hg and Tl organometallic compounds in [4, 5], are also possible here. There is, therefore, a need for a detailed study of these possibilities. The present paper will outline the results of a study of the kinetics of these processes, a work in which kinetic and activational parameters for reactions of onium compounds with metals have been determined for the first time.

The choice of kinetic experiments for this work was made difficult by the possibility of side reactions, particularly in view of the reported appearance of ArCl and calomel in the reaction products [6]. In general, the stoichiometry of the  $Ar_2IX + Hg$  reactions did not conform to Eq. (1). It was therefore necessary to choose the working conditions (and especially the temperature) so as to reduce effects from the side reactions (3) and (4) to a minmum

$$2Ar_2IX + 2Hg \rightarrow 2ArI + Hg_2X_2 + ArAr$$
(3)

$$Ar_2IX \rightarrow ArI + ArX$$
 (4)

Experiment showed that neither diphenyliodonium chloride (DC) nor bromide (DB) would undergo appreciable thermal breakdown through reaction (4) in MeCN solution at 70°C. Under these conditions, reaction (3) was also of minor significance. This last conclusion followed from a quantitative analysis of the products and a test of the stoichiometry of reaction (1). Over the interval from 20 to 70°C, the range of interest here, the composition of the reaction products was essentially independent of the temperature. A more detailed study showed that 94% of the DC in a  $10^{-3}$  mole/liter MeCN solution would undergo reaction in 22 h at 45°C. This figure was arrived at both through measurement of the residual DAS and through determination of the amount of product iodobenzene. The data of Table 1 indicated that reaction (1) was the principal process occurring at 70°C, side reactions having scarcely any effect on the measured reaction rate at this temperature.

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TABLE 1. Yield (% of theoretical) of Products in the  $Ph_2IX - Hg$ Reaction, in MeCN Solution at 45°C (calculated from the amount of reacted iodonium salt)

X	PhHgX	$Hg_2X_2$	PhI	PhH	PhPh	PhX
Cl Br	89–92 Not dete	10-11 ermined	100 100	1,4 1,4	$4-5 \\ 6-7$	Trace

TABLE 2. Rate Constants for Reactions of the Diaryliodonium Chlorides  $(YC_6H_4)_2ICI$  with Metallic Hg in MeCN Solution at 50°C (initial salt concentration  $10^{-3}$  mole/liter)

Y	p-CH <sub>3</sub> O	p-CH <sub>3</sub>	p-GI	н	p-Cl, $m$ -NO <sub>2</sub>	m-NO <sub>2</sub>
k <sub>1</sub> · 10 <sup>4</sup> sec <sup>-1</sup>	$1,40\pm0,11$	$1,71\pm0,09$	$2,26\pm0,10$	$2,46\pm0,20$	$3,17\pm0,09$	$3,50\pm0,13$

TABLE 3. Rate Constants  $(k_1)$ , Activation Energies  $(E_a)$ , and Activation Entropies  $(\Delta S_{298^{\circ}K})$  for the Reactions of Ph<sub>2</sub>ICl and Ph<sub>2</sub>IBr with Metallic Hg in MeCN Solution

·	h <sub>1</sub> ·10 <sup>4</sup> , sec <sup>-1</sup>						17	
Ph <sub>2</sub> IX	20°	30°	40°	50°	60°	70°	kcal/ mole	ΔS <sub>298 K</sub> . e.u.
X=Cl	$0,89\pm0,03$	1,29±0,06	1,80±0,15	2,46±0,20	3,16±0,20	$3,36 \pm 0,09$	6,25	-57,7
X=Br	$2,19\pm0,09$	$2,99 \pm 0,11$	$4,31\pm0,10$	5,37±0,13	$6,82\pm0,17$	$7,94{\pm}0,09$	5,80	-57,5

Since it had been reported that the DAS decompose on heating in organic solvents [4], the stability of each compand covered by this work was tested before kinetic measurements were carried out on it. Correction for DAS thermal breakdown was introduced in treating the kinetics of type (1) reactions, at 60 and 70°C in the case of the DC, and at 40–70°C in the case of the DB. The kinetics of the diaryliodonium substituted chloride reactions were studied at  $50^{\circ}$ C.

The kinetics were followed by measuring the DAS consumption through UV spectroscopy [7]. Earlier experiments had shown that the reaction products would not interfere with the quantitative determination of the Ph<sub>2</sub>IX content of these systems. Usually, each reaction was allowed to run to 70% completion. In the case of the DC reactions, it was shown that the rate constant was not affected by altering the initial DC concentration, at least over the range from  $1 \cdot 10^{-3}$  to  $5 \cdot 10^{-3}$  mole/liter. The kinetic curves could be described by a first-order rate equation (Fig. 1). Rate constants were calculated from the equation  $k = (2.303/\tau) \cdot \log C_0/C$ , the results being as shown in Tables 2 and 3.

It can be seen from Table 2 that the effect of introducing substituents into the Ar<sub>2</sub>ICl benzene ring was minimal. A graph showing the variation of log k<sub>1</sub> with the substituent  $\sigma$  constant (the sum  $\sigma_{p-Cl} + \sigma_{m-NO_z}$  was plotted in the case of the p-chloro-m-dinitro derivative) is given as Fig. 2. From the value of the reaction constant,  $\rho = +0.39$ , it was concluded that these reactions were insensitive to alterations in the substituent elec-tronic effect, and nucleophilic with respect to the organic substrate.

This last conclusion would be consistent with both a one-electron transfer mechanism (SET-mechanism) [Eq. (2)] and a penetration mechanism [Eq. (5)] with the Hg atom considered as a nucleophilic carbenoid

$$Ar \xrightarrow{\Psi} Ar \xrightarrow{H} Ar$$

The schemes of (2) and (5) show reaction proceeding through nucleophilic Cl<sup>-</sup> anion interaction, it being known that halide ions promote reaction (1) [8], while the diaryliodonium borofluorides do not react with mercury [9]. Still another analogy can be set up here. The alkylmercury perchlorates, especially the perchlorates of secondary and tertiary alkyl compounds, readily lose metallic mercury and pass over into carbocation form [10]



Fig. 1. Typical kinetic curves for the reactions of  $Ph_2ICI$  (1) and  $Ph_2IBr$  (2) with metallic mercury in acetonitrile solution at 20°C, and corresponding semilogarithmic anamorphic curves, (3) and (4).

Fig. 2. Variation of the rate of breakdown of the substituted diaryliodonium chlorides  $(YC_6H_4)_2ICl$  under the action of mercury in acetonitrile solution at 50°C, with the  $\sigma$  constant of the substituent  $Y = p-OCH_3$  (a);  $p-CH_3$  (b); H (c); p-Cl (d);  $m-NO_2$  (e);  $p-Cl-m-NO_2$  (f).

$$AlkHgClO_4 \rightarrow Alk^{\oplus} + Hg^0 + ClO_4^{\odot}$$

The alkylmercury halides are, on the other hand, completely stable. It could be that complex (I) in the mechanism of (5) is established by Cl<sup>-</sup> ion coordination, an effect which would be lost if the Cl<sup>-</sup> were replaced by a  $BF_4^-$  ion.

If it were assumed that the Hg atom functions as an electrophilic carbenoid, the reaction mechanism could be described by the following scheme:

$$Ar \xrightarrow{\bigoplus}_{I-Ar} Ar \xrightarrow{\Theta}_{Cl} Ar \xrightarrow{\downarrow}_{Hg} A$$

Although the key steps in the mechanism of (5) and (6), namely  $(I) \rightarrow (II)$  and  $(III) \rightarrow (IV)$ , each proceed through a cyclic transition state, the first is a two-electron, and the second a four-electron, process. Thus, the  $(I) \rightarrow$ (II) reactions recalls a Wagner-Meerwein rearrangement, and the  $(III) \rightarrow (IV)$  reaction a Stevens or Wittig rearrangement. It is well-known fact that rearrangements of the latter type proceed through radical pair formation [11]. It was, therefore, necessary to consider the possibility that the reactions in question here might also proceed through a radical mechanism

 $(III) \rightleftharpoons \begin{bmatrix} Cl & Cl & \\ \downarrow & \downarrow \\ :I - Ar \leftrightarrow :I - Ar \\ Ar \cdot \downarrow & Ar \cdot \downarrow \\ \cdot Hg & \cdot Hg \end{bmatrix} \rightleftharpoons \begin{bmatrix} Cl & \\ \downarrow \\ I - Ar \\ Ar - Hg \\ Ar - Hg \end{bmatrix} (IV)$ 

The mechanism of (6) would be consistent with the observed substituent effect if (III)  $\rightarrow$  (IV) were the slow step in the scheme, and the Hg-containing radical involved in radical pair (V) formation were nucleophilic.

Interesting results were obtained from study of the temperature variation of the rates of DC and DB breakdown under the action of mercury. The activation energies of Table 3 were obtained from  $\log k_1 \text{ vs } 1/T$  Arrhenius plots. Activation entropies were calculated from the well-known equation  $\Delta S^{\neq} = 4,576 \log (A/T) - 49.21$ . The fact that the values of  $\Delta S^{\neq}$  were both large and negative suggested that the transition state for the limiting step in the mechanism was more highly ordered than the initial state. Although the activation energies were not large, they were still higher than the activation energy for diffusion; since the reaction rate was sensitive to alteration in the nature of the substituent, diffusion could not have been the limiting step here.

In giving preference to the one-electron transfer mechanism, one must ignore the mechanisms of (5) and (6), either of which would be consistent with low activation energies and high, negative activation entropies. Mechanism (5) would seen to be more probable than (6), since metallic mercury behaves as a nucleophilic, rather than electrophilic, carbenoid in its reactions with Hg [4] and Tl [5] organic compounds.

#### EXPERIMENTAL

The diaryliodonium salts used here had been prepared by the methods of [12]. The iodobenzene, benzene, and diphenyl were determined on an LKhM-8M chromatograph equipped with a flame-ionization detector, using a 1.5 m  $\times$  3 mm glass column packed with a 5% solution of triscyanoethoxypropane on Celite-545, with N<sub>2</sub> acting as the carrier gas at 20 ml/min. Each compound was identified by comparison with standards. Compositions were calculated relative to internal standards, bromobenzene in the case of the DC and chlorobenzene in the case of the DB. Best separations were obtained at 70°C in the case of the PhH-PhBr-PhI mixtures, and at 100°C in the case of the PhI-PhPh mixtures.

The yield of organomercury compound was determined from spectrophotometry of the dithiozone complex, working with an SF-16 spectrometer system. Interference from calomel in the PhHgCl determination was avoided by following the method of acid extraction from 3 N HCl described in [13]. Here the total amount of Hg products, PhHgCl + calomel, was determined as the Hg(II) dithiozonate through spectrophotometry of the HClacidified reaction mixture [14]. The calomel content of the reaction mixture was then obtained by difference.

Reaction Kinetic Studies. Reactions were carried out in a 60-ml cell whose temperature was held constant to within  $\pm 0.5$ °C; into this cell there was rapidly loaded 30 ml of a previously thermostated MeCN solution of the diaryliodonium salt in question. The mercury surface area was 13 cm<sup>2</sup>. Reactions were carried out with the solution stirred at 600-900 rpm\* the arrangement being such that the stirrer was located above, but not in contact with, the mercury, thus assuring that the surface area of the latter remains constant. Reaction was followed by removing samples (1 ml) every 10-20 min, depending on the reaction rate. The iodonium salt content of each sample was determined by the procedure of [7].

#### CONCLUSIONS

1. A study has been made of the kinetics of the reactions of diaryliodonium salts with metallic mercury in acetonitrile solution.

2. The reactions of the diaryliodonium chlorides with mercury are insensitive to changes in the substituent in the benzene ring of the iodonium salt.

3. A study has also been made of the temperature variation of the rates of decomposition of diphenyliodonium chlorides and bromides under the action of mercury in acetonitrile solution. Activation parameters have been obtained for these reactions.

4. Discussion is given of possible mechanisms for the reactions of these salts with mercury.

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# \*The reaction rate remained constant over this range of stirring rates.