PROTODEMERCURATION OF HETEROANNULAR MERCURY DERIVATIVES OF HALOFERROCENES

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The reactivity of halogens in the ferrocenyl ring differs from that in the phenyl ring. Therefore, studies devoted to the quantitative evaluation of the reactivity of the haloferrocenes are of great importance. Up to the present time, the influence of halogens on the rate of deuteroexchange [1] and on the dissociation constants of heteroannular ferrocenecarboxylic acids [2] had been studied.

In this work we investigated the influence of halogens upon the rate of protolysis of mercury derivatives of ferrocene. We measured the rates of protodemercuration of hydrochloric acid in 90% (by volume) aqueous dioxane of heteroannular mercury derivatives of haloferrocenes: 1-chloro-(1'-chloromercury)ferrocene, di-[1-(1'-chloroferrocenyl)]mercury, 1-bromo-(1'-chloromercury)ferrocene, and di-[1-(1'-bromoferrocenyl)]mercury. We had earlier conducted the protolysis of chloromercuryferrocene and diferrocenylmercury [3].

A comparison of the rates of protodemercuration (Table 1) showed that heteroannular chloro- and bromo-substituted mercury derivatives of ferrocene react 14 and 18 times more slowly than diferrocenylmercury, respectively. The introduction of halogens into the diphenylmercury molecule leads to a decrease in the rate of protodemercuration by 8-fold for di-(p-bromophenyl)mercury and 5.5-fold for di-(p-chlorophenyl)mercury, while for di-(m-chlorophenyl)mercury the decrease in the rate is 33-fold [4]. Consequently, halogens as substituents in the ferrocenyl ring exert a stronger deactivating influence than the phenyl ring from the para-position, and weaker effect from the meta-position. Such an influence of the halogens is explained by their negative inductive effect. Strengthening the electron acceptor influence of the halogens usually involves a decrease in the +C effect of these substituents. The stronger influence of electron acceptor substituents in the ferrocenyl ring in comparison with the para-position of the phenyl ring has been noted repeatedly and is probably due to the well-known fact that the ferrocenyl ring possesses stronger electron donor properties than the phenyl ring.

TABLE 1

Compound*	Reaction temp., °C	k_2 mole^{-1} $\times$ min^{-1}·liter	$E^{\neq}$, kcal/mole	$\Delta S^{\neq}$, entropy units	Compound*	Reaction temp., °C	k_2 mole^{-1} $\times$ min^{-1}·liter	$E^{\neq}$, kcal/mole	$\Delta S^{\neq}$, entropy units
(BrC$_5$H$_4$FeC$_5$H$_4$)$_2$Hg	20 25 30 35	2,43 4,99 9,07 18,67	23,1	+12,0	BrC$_5$H$_4$FeC$_5$H$_4$HgCl	30 35 40 45	0,0559 0,1061 0,2348 0,3291	23,5	+ 3,8
(ClC$_5$H$_4$FeC$_5$H$_4$)$_2$Hg	20 25 30 35	3,13 7,56 14,34 30,58	25,8	+21,9	ClC$_5$H$_4$FeC$_5$H$_4$HgCl	30 35 40 45	0,0810 0,1428 0,3268 0,5474	25,1	+ 9,1

*For the protolysis of diferrocenylmercury and chloromercuryferrocene under the same conditions, the activation energies are equal to 18.6 and 19.9 kcal/mole, while the entropies of activation are +1.6 and −3.4 entropy units, respectively [3].

From Table 1 it is evident that bromo-derivatives react approximately 1.5 times as slowly as mercury derivatives of chloroferrocene. Exactly the same order of change in the reactivity is observed in the aromatic series, where protolysis of di-(p-bromophenyl)mercury also proceeds approximately 1.5 times more slowly than cleavage of di-(p-chlorophenyl)mercury [4]. Protolysis of nonsymmetrical halo-substituted mercury derivatives, as usual, proceeds more slowly than the protolysis of symmetrical derivatives (approximately 180 and 160 times more slowly for the chloro- and bromo-derivatives, respectively).

The higher activation energies for the protolysis of halosubstituted derivatives in comparison with the activation energies of the protodemercuration of unsubstituted chloromercuryferrocene and diferrocenylmercury [3] (see Table 1) are probably due to the electron acceptor properties of the halogens as substituents. The activation energies for the chloroderivatives are higher than the corresponding values for the bromoderivatives. However, the higher entropies of activation for the chloroderivatives lead to the fact that chloroferrocenylmercury derivatives are more reactive than the bromoderivatives. The activation energies for the symmetrical and corresponding nonsymmetrical derivatives practically coincide (see Table 1), and their different reactivities are probably due only to entropy factors. The entropies of activation of the protodemercuration of chloro-substituted mercury derivatives are substantially higher than for the nonsubstituted derivatives. Of a number of factors that can cause such a substantial increase in the entropy of activation, the most probable seemed to us to be solvation effect: the substantially greater solvation of components with electron acceptor substituents in the ground state than in the transition state, by solvents possessing a free electron pair, in comparison with the unsubstituted compounds.

EXPERIMENTAL

The protodemercuration procedure was analogous to [3].

The reaction rates possess a total second order (first order with respect to each of the reagents). The rate constants are averages of a minimum of 3 measurements. The rate constants and activation energies were calculated by the method of least squares. The accuracy of the determination of the rate constants is ±5%, and that of the activation energies ±6%.

1-Chloro-(1'-chloromercury)ferrocene, di-[1-(1'-chloroferrocenyl)]mercury, and di-[1-(1'-bromoferrocenyl)]mercury were synthesized according to the procedure described in the literature [5]. 1-Bromo-(1'-chloromercury)ferrocene was synthesized according to a procedure analogous to that described for the production of 1-chloro-(1'-chloromercury)ferrocene [5], yield quantitative, m.p. 149.5-150.5° (acetone). Found %: C 24.34, 24.40; H 1.94, 1.80. $C_{10}H_8ClBrHgFe$. Calculated %: C 24.09; H 1.61.

CONCLUSIONS

1. The protolysis of 1-chloro-(1'-chloromercury)ferrocene, 1-bromo-(1'-chloromercury)ferrocene, di-[1-(1'-chloroferrocenyl)]mercury, and di-[1-(1'-bromoferrocenyl)]mercury was conducted.

2. The rate of protolysis of mercury derivatives of haloferrocenes is lower than that of chloromercuryferrocene and diferrocenylmercury. The protolysis of nonsymmetrical mercury derivatives of haloferrocenes is slower than that of the corresponding symmetrical derivatives.

LITERATURE CITED

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