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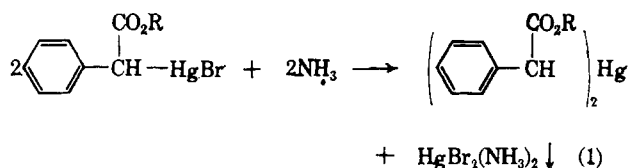
## Ammonia Symmetrization of Organomercuric Halides

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An examination of the results presented by previous workers for the symmetrization of alkylmercuric bromides by ammonia shows that their proposed mechanism does not follow the reported kinetics. Also, the very rapid formation of insoluble mercuric bromide-ammonia complex negates this mechanism. Therefore, the general conclusions regarding  $S_E2$  reactions derived by these workers from symmetrization are invalid. Various mechanisms for the reaction are discussed; however, it is shown that the previous kinetic evidence is internally inconsistent and that a reinvestigation of the kinetics is necessary before a mechanism can be assigned.

Symmetrization of alkylmercuric halides by ammonia had been extensively investigated by Reutov and his co-workers.<sup>1</sup> Esters of  $\alpha$ -bromomercuriphenylacetic acid readily react and they have been widely used.



In chloroform solution, the reaction has the stoichiometry indicated in eq. 1; the mercuric bromide-ammonia complex precipitates as the symmetrization proceeds.<sup>2</sup>

The stereochemistry of this reaction has been demonstrated by Nesmeyanov, Reutov, Yang-Chieh, and Ching-Chu.<sup>3</sup> Retention of configuration at the carbon seat of reaction was observed.<sup>4</sup> Kinetic studies have demonstrated that with constant initial concentration of ammonia ( $\sim 1 M$ ), and initial alkylmercuric bromide concentration in the range 0.0085 to 0.068  $M$ , the reaction is second order with respect to alkylmercuric bromide.<sup>1,5</sup> Individual experiments were found to obey simple (pseudo) second-order kinetics, and invariant rate constants were obtained upon changing the initial concentration of alkylmercuric bromide. In addition, it was shown that the half-lives of the reactions give comparable second-order rate constants from the equation  $k = 1/at_{1/2}$ .

Similarly, a determination of initial reaction velocities with constant alkylmercuric halide concentration (0.068  $M$ ) and variable ammonia concentration (0.1 to 0.635  $M$ ) demonstrated that the reaction is also second order in complexing agent.<sup>6</sup> The order with respect to ammonia was primarily determined by observing the initial changes in rate, and the initial rates corresponded very closely to the expected behavior for second-

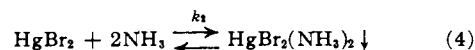
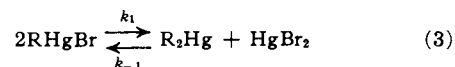
order dependence in ammonia. (The reactions at very low ammonia concentration are reported not to go to completion.)

In these latter kinetic studies, the highest ammonia concentration used was 0.635  $M$ , but, in the majority of later studies in which the effect of substituents on rate were investigated, the ammonia concentration was usually  $\sim 1 M$ . Unfortunately, it is not possible from the data presented to compare rate constants at these two concentrations. The following evidence is available to indicate that no change in rate-controlling step occurs: (1) A complete change in rate-controlling step cannot be expected by changing the concentration by less than a factor of two; (2) no statement was found in any of the papers suggesting that a change in rate-controlling step occurs; and (3) the equations presented in later papers were similar to those given in the papers which reported the kinetics of the reaction.

On the basis of these results, Reutov and co-workers concluded that the reaction is second order in alkylmercuric halide and second order in ammonia. This rate behavior is illustrated in eq. 2.

$$\text{rate} = k[\text{RHgX}]^2[\text{NH}_3]^2 \quad (2)$$

The mechanism suggested by Reutov and co-workers<sup>1,5,6</sup> to accommodate these observations is shown.



The step believed to be rate controlling was not explicitly stated by Reutov and co-workers.<sup>1,5-7</sup> One possibility is that eq. 3 is rate determining; however, this obviously cannot be the case because the second-order dependence on ammonia cannot then be explained even on a casual basis. The kinetic order which would be obtained if eq. 3 is rate-controlling is rate =  $k[\text{RHgBr}]^2$ .

In these papers, Reutov and co-workers repeatedly stated that symmetrization (eq. 3) occurs in a rapid, reversible reaction without the assistance of complexing agent. It was stated that the role of the ammonia is to bind the mercuric halide and thereby shift equilibrium 3 to the right.<sup>1,6</sup> It was also stated that the reaction does not go to completion at low ammonia concentrations and therefore reaction 4 must also be reversible. The bimolecular dependence on alkylmercuric halide was explained as arising from equilibrium 3 and the bimolecular dependence on ammonia from formation of

(7) In ref. 8a, it was casually mentioned that eq. 3 is rate controlling, but no evidence supporting this contention was ever given.

(1) O. A. Reutov, I. P. Beletskaya, and R. E. Mardaleishvili, *Proc. Acad. Sci. U.S.S.R.*, **116**, 901 (1957). Translations of the Russian are cited herein whenever available; however, the original papers in Russian have been rigorously examined for accuracy of translation for each reference made to the work.

(2) The precipitated complex has been described (ref. 1) as being free of starting material and organic product.

(3) A. N. Nesmeyanov, O. A. Reutov, W. Yang-Chieh, and L. Ching-Chu, *Bull. Acad. Sci. U.S.S.R.*, **1280** (1958).

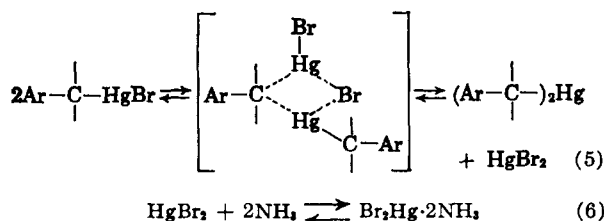
(4) An earlier observation of racemization [A. N. Nesmeyanov, O. A. Reutov, and S. S. Poddubnaya, *ibid.*, **753** (1953)] has been ascribed to optical instability of alkylmercuric halide under the more vigorous conditions which were used.

(5) O. A. Reutov, I. P. Beletskaya, and R. E. Mardaleishvili, *Zh. Fiz. Khim. SSSR*, **33**, 152 (1959).

(6) O. A. Reutov, I. P. Beletskaya, and R. E. Mardaleishvili, *Russ. J. Phys. Chem.*, **33**, 240 (1959); *Zh. Fiz. Khim. SSSR*, **33**, 1962 (1959).

the complex (eq. 4). The reason proposed for the bimolecular dependence on ammonia concentration clearly conveyed the interpretation that the second step is rate controlling. No evidence was ever found indicating any other step to be rate controlling.

Although it was repeatedly stated that the first step in the reaction is reversible, in subsequent papers, Reutov and co-workers have ascribed various rate effects observed for symmetrization to the demands of the transition state for this equilibrium (eq. 5).<sup>8</sup> Clearly, this interpretation is inconsistent with the proposal that the reaction is second order in the ammonia concentration.



Reaction rates in this instance would vary with the position of the equilibrium in eq. 5, but would in no way reflect the nature of the transition state for the equilibrium. Therefore, the conclusions drawn in this series of papers regarding the nature of S<sub>E</sub>2 reactions are untenable.

Furthermore, the suggested mechanism would not follow the observed kinetic expression 2, but rather eq. 7. (At high ammonia concentrations, the reaction goes to completion and therefore the second step is not reversible under these conditions.)

$$\text{rate} = k_2 K_1 [\text{RHgBr}]^2 [\text{NH}_3]^2 / [\text{R}_2\text{Hg}] \quad (7)$$

It is important to note that in this correct form of the kinetic expression for the proposed mechanism, the first step of the reaction is represented by an equilibrium constant ( $K_1 = k_1/k_{-1}$ ) and not a rate constant and therefore the over-all rate constant for the reaction would give no information regarding the transition state of this equilibrium.<sup>9</sup>

In order for the kinetic expression (eq. 7) for the proposed mechanism to be operating, it is necessary that inhibition by product occurs as it is formed in the reaction.<sup>2,5</sup> In the determination of the order with respect to alkylmercuric bromide (pseudo-second-order conditions), the reactions were followed well past 50% reaction and the extensive kinetic data show no indication of inhibition by product. (However, see the discussion of the effect of added R<sub>2</sub>Hg on rate given below). Perhaps the simplest procedure for illustrating the difference in expected behavior for eq. 2 and 7 is to calculate rate constants from reaction half-lives.

(8) (a) O. A. Reutov and I. P. Beletskaya, *Proc. Acad. Sci., USSR*, **131**, 333 (1960); (b) O. A. Reutov, I. P. Beletskaya, and G. A. Artamkina, *J. Gen. Chem. USSR*, **30**, 3190 (1960); (c) O. A. Reutov, *Record. Chem. Progr.*, **32**, 1 (1961); (d) I. P. Beletskaya, G. A. Artamkina, and O. A. Reutov, *Izvest. Akad. Nauk SSSR*, 765 (1963); (e) I. P. Beletskaya, G. A. Artamkina, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **149**, 90 (1963); (f) O. A. Reutov, I. P. Beletskaya, and G. A. Artamkina, *Russ. J. Phys. Chem.*, **36**, 1407 (1962).

(9) In order for the observed rate constant to reflect information regarding the nature of the transition state of the first step, it is necessary that this step be rate controlling in the proposed mechanism. This can only be the case if the rate is independent of the ammonia concentration; however, in every instance where reference was made to the effect of ammonia concentration on rate, it was clearly stated that the reaction is second order in the ammonia concentration.

With the high ammonia concentrations used, these equations reduce to eq. 8 and 9, respectively, wherein  $x$

$$\text{rate} = k_2' [\text{RHgX}_2]^2 = k_2' [a - x]^2 \quad (8)$$

$$\text{rate} = \frac{k'' [\text{RHgX}_2]^2}{[\text{R}_2\text{Hg}]} = k'' \frac{[a - x]^2}{x} \quad (9)$$

designates the amount of product formed and  $a$  the initial concentration of the alkylmercuric halide. From eq. 10, the integrated form of eq. 9, the rate constant is readily deduced to be  $k'' = 0.308/t_{1/2}$ . It is interesting to note that the half-lives of reactions 5 and

$$k''t = \frac{x}{a - x} + \ln \frac{a - x}{a} \quad (10)$$

6 (kinetic expressions 9 and 10) would be independent of initial concentrations of alkylmercuric halide. However, the reported kinetic order (eq. 8) would follow the expected dependency for second-order behavior ( $k' = 1/at_{1/2}$ ).

In Table I, a comparison of rate constants calculated from half-lives with varying initial RHgBr concentrations, but constant NH<sub>3</sub> concentrations, are shown. These data were calculated using the appropriate expressions deduced from eq. 8 and 9. The relative constancy of  $k_2'$  as compared to  $k''$  shows that the data fit eq. 8 more satisfactorily than eq. 9. Even stronger evidence for this is found from consideration of data for individual kinetic runs. Thus, it appears definite from consideration of the data presented by Reutov and co-workers that the observed kinetics are inconsistent with their proposed mechanism.

TABLE I<sup>10</sup>

[RHgX] <sub>init</sub> , (a), × 10 <sup>2</sup>	t <sub>1/2</sub> , sec.	k'' = 0.308/t <sub>1/2</sub> , sec. <sup>-1</sup> × 10 <sup>20</sup>	k <sub>2</sub> ' = 1/at <sub>1/2</sub> , l. mole <sup>-1</sup> sec. <sup>-1</sup>
6.80	136	2.26	1.08
5.44	190	1.62	0.97
3.40	305	1.01	.97
2.72	400	0.77	.92
1.70	400	0.77	1.47

[NH<sub>3</sub>]<sub>0</sub> = constant ~1 M

<sup>a</sup> Calcd. using the appropriate form of eq. 9 and 10. <sup>b</sup> Calcd. using the appropriate form of eq. 8.

We felt it highly unlikely that complex formation or precipitation of the complex would be the rate-determining factor in the ammonia symmetrization. A very simple test of this hypothesis was devised; chloroform solutions of mercuric bromide and ammonia were prepared and admixed. The *instantaneous precipitation of complex* even at mercuric bromide concentration less than 10<sup>-5</sup> M attests to the rapidity of eq. 4. From these crude experiments, it appears that the solubility of the complex is ca. 10<sup>-6</sup> M.

(10) The units used in Table I are those reported by Reutov, *et al.*;<sup>8</sup> however, these dimensions differ in various references. For example, in one paper, for comparable concentrations, equivalent extents of reaction are discussed in terms of fractions of an hour (~0.5 hr.) and seconds (20–25 sec.). In an effort to clarify this apparent contradiction, the raw experimental data were examined; there, unfortunately, times are reported in degrees centigrade. Re-evaluation of the results in the papers cited herein is sometimes impossible because dimensions are commonly omitted. For the tenacious reader who attempts to interpret the results in ref. 5, it will help to note that the quantities plotted in Fig. 1 and 2 are probably (C<sub>0</sub> - C)/6.8 × 10<sup>-5</sup> rather than C<sub>0</sub> - C. Apparently, only one calibration curve was obtained (Fig. 1) and this appears to be derived from the infinity values obtained in the kinetic runs of Table I. The quantity plotted on the y-axis of Fig. 3 appears to be in units of 6.8 × 10<sup>-5</sup> (C<sub>0</sub> - C)/C<sub>0</sub>C.

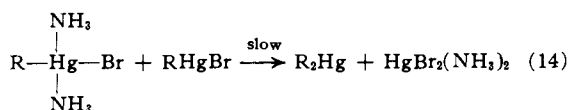
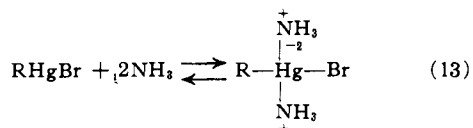
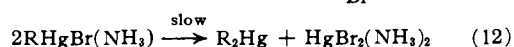
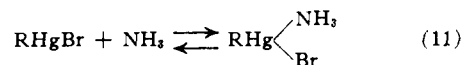
The precipitate was formed as a finely divided or colloidal material. In no instance was an increase in cloudiness observed on standing. Thus, instantaneous complex precipitation was observed in concentration ranges which amount to very small fractions of the initial concentrations used by Reutov in his kinetic studies (TABLE II).

(TABLE II)

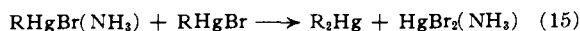
CONCENTRATION OF REAGENTS AFTER MIXING		
[NH <sub>3</sub> ], M	[HgBr <sub>2</sub> ] × 10 <sup>3</sup> , M	Precipitation
1.1	3.1	Instantaneous
1.1	0.6	Instantaneous
1.1	.12	Instantaneous
1.2	.05	Instantaneous
1.2	.007	Instantaneous (faint)
1.2	.0016	?
1.2	.0009	No visible colloid
0.55	1.8	Instantaneous
.01	0.05	Instantaneous
.002	0.050	Very fast or instantaneous

As discussed above, the kinetic results of Reutov and co-workers are not in accord with their proposed mechanism for either step being rate controlling. The observation of the fast rate of precipitation of mercuric bromide-ammonia complex provides further evidence against this mechanism. Since the reverse reaction of eq. 3 ( $R_2Hg + HgBr_2 \rightarrow 2RHgBr$ ) is sufficiently slow<sup>11</sup> that its rate can be determined by conventional kinetic methods, it is unlikely that this process is faster than the reaction of mercuric bromide and ammonia.

Two possible alternate mechanisms which can account for the observed kinetic order both involve ammonia-complex formation with the alkylmercuric halide<sup>12</sup>



Between these, the latter seems more probable; eq. 12, which represents cleavage of monoammonia complex by monoammonia complex, would more likely be supplanted by cleavage of this complex by simple alkylmercuric halide (eq. 15). The uncomplexed material is



expected to be a stronger electrophile than the complexed compound, and hence the relative importance of reaction 12 and 15 would depend on their rate constants and the position of equilibrium 11. Reactions 11 and 15 would yield first-order dependence on the ammonia concentration.

Doubly ammonia-complexed alkylmercuric halide (eq. 13) should be very susceptible to electrophilic at-

(11) The rates have not been determined for the alkyl groups used by Reutov and co-workers.

(12) The mechanism shown in eq. 11 and 12 was briefly mentioned by Reutov and co-workers as a possibility but was rejected on the grounds that symmetrization of these compounds also occurs in the presence of diphenylmercury.  $(C_6H_5)_2Hg + RHgBr \rightarrow R_2Hg + 2C_6H_5HgBr$ .

tack because of the high charge density on mercury and carbon. Unfortunately, without prior knowledge of the position of equilibrium 13, it is not possible to derive conclusions regarding the nature of the transition state from the observed rate constants. The very factors which tend to favor reaction 13 will usually be expected to hinder reaction 14.<sup>13</sup>

In an attempt to establish the generality of complex formation of alkylmercuric halides, *sec*-butylmercuric bromide (which does not undergo symmetrization under these conditions) was treated with ammonia in carbon tetrachloride solution. A colorless precipitate was formed immediately. This material dissolved readily in chloroform, unlike the mercuric bromide-ammonia complex. An effort was made to determine the number of ammonia ligands attached to mercury by filtering and drying the precipitate, but loss of ammonia occurs so rapidly in the solid state that analysis was impossible.<sup>14</sup> Nevertheless, the formation of a complex was clearly demonstrated and may thus be called on as a readily available intermediate in any reaction under comparable conditions. It is to be noted, however, that the precipitate which forms under these conditions does not necessarily contain the same ratio of reagents as the reactive intermediate in symmetrization.

As already noted, substantial evidence is found in the kinetic results of Reutov and co-workers that no rate depression by product ( $R_2Hg$ ) occurs. It was also shown that the precipitate is free of this product. However, in somewhat limited studies, when this material was added from an external source at the start of the reaction, the initial rates were found to be inversely proportional to the amount of added  $R_2Hg$ . Clearly, this is contrary to the previous kinetic work. However, it is difficult to assess these latter data, since it cannot be deduced from the presented values whether the amount of  $R_2Hg$  added was limiting or swamping; the amounts presented in tabular form differ from the amounts stated in the text by a factor of one hundred (a factor of ten in the English translation). Because of the contradiction with the more extensive kinetic data and the doubt as to concentration, further evaluation of these results is not possible at this time.

## Experimental

Carefully purified chloroform was used in the preparation of the solutions of mercuric bromide (reagent grade) and anhydrous ammonia. Concentrations of mercuric bromide and ammonia were determined by evaporation of solvent and weighing residues and by titration with acid to the bromophenol blue end point, respectively.

Solutions were prepared by mixing measured volumes of these standard solutions; the precipitated complex was observed visually and no apparent increase was noted on standing overnight.

Since Reutov and co-workers did not state the purity of their chloroform, parts of the experimental work were repeated using 0.75% ethanol. Identical results were obtained.

**Acknowledgment.**—Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

(13) The suggestions as to mechanisms proposed here are derived utilizing the most heavily documented experimental results of Reutov and co-workers, but there are contradictions in the kinetic results which cannot be reconciled. Our view is that these proposals are tentative and that a reinvestigation of the kinetics is required, especially in view of the reversibility of the reaction, before definite conclusions are warranted.

(14) A more rigorous investigation of these complexes is being carried out.