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Salt effects in the mercuration of unsaturated compounds. Kinetic evidence for the formation of ion pairs and a solvated ion

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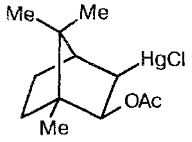
The kinetics of mercuration of bornylene and cyclohexene in different solvents in the presence of NaOAc and $LiClO_4$ has been investigated. Addition of NaOAc sharply decreases the rate of addition reactions of mercuric acetate to bornylene and cyclohexene in alcohols; the main direction of the mercuration of bornylene is the formation of acetoxy-adducts, and the yield of solvo-adducts decreases from 76 % in the absence of NaOAc, to 19 % in the presence of the salt ($4 \cdot 10^{-3}$ mol L^{-1}). A reaction scheme involving the participation of intermediate ion pairs and a solvated mercurinium ion is suggested and confirmed by a steady-state concentration method. The influence of NaOAc on the rate of the reaction and on product formation is realized through the common ion effect.

Key words: bornylene, mercuration, kinetics; salt effect; common ion effect; ion pair, solvated ion; reaction mechanism.

Although a great number of works deal with investigating the mechanism of the reactions of mercury salts with alkenes, many principal aspects are still under discussion.[1] In general, the reaction route depends on the nature of the reagent, the solvent, the acidic and basic properties of additives, the substrate structure, and some other factors,[2–9] but the mechanisms of these influences have not yet been studied much.

To elucidate the reaction mechanism, including the mechanisms of the organometallic reactions, the method of salt effects[10] is effective. Salt effects are also characteristic of mercuration of alkenes. It is known that additives of such salts as group I metal acetates and halides may change the reaction route, as well as decrease its rate greatly.[2,6,11–15] In the case of certain alkenes, *i.e.*, those with a strained double bond, the formation of solvo-adducts is substantially or completely suppressed.[2,13–15]

The mechanism of the action of salt additives has not yet been specifically investigated. The reported data only support the conclusion that the salt effect is closely associated with the mercuration mechanism[14]. With this in mind, we have investigated the nature of the salt effect using, as an example, the reaction of $Hg(OAc)_2$ with bornylene (**1**) and cyclohexene (**2**) in various solvents (MeOH, EtOH, Pr^nOH, MeCOOH) and with salt additives such as NaOAc and $LiClO_4$. We chose compound **1** as a model reagent, because it affords a mixture of regioisomers, the ratio between which provides additional information about the reaction mechanism.[1] The data about products **3**—**6**, which are formed by mercuration of **1** in the absence of salt, and the ratio between them have been reported previously.[1]



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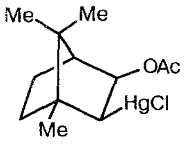

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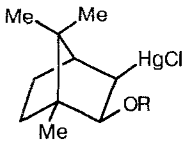

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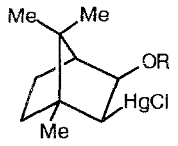

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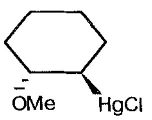

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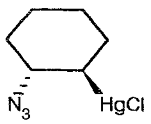

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R = Me, Et, Pr^n

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 819—826, May, 1994.

Mercuration of compound **2** has been studied in many works.[16] It was found that in alcohols and water-organic media the reaction can only proceed in a solvomercuration direction to give *trans*-adduct **7**.

Experimental

Analysis by NMR spectroscopy and GLC was carried out as described previously.[1] For kinetic studies, an SP-46 spectrophotometer was used. The purity of reagents and solvents was 99.0—99.8 %.

The ratio between the products of the mercuration of **1** in the presence of NaOAc was found at concentrations $[\text{Bornylene}] = [\text{Hg(OAc)}_2] = 0.1$ mol L^{-1}.

The reaction rate was evaluated by monitoring the changes in $[\text{Hg(OAc)}_2]$, which were recorded by spectrophotometry.[17] An aliquot of the reaction solution (0.2—2 mL depending on the concentration of the reagents) was added to a $2.5 \cdot 10^{-3}$ *M* solution of KBr in a MeOH—H_2O (0.91:0.09) mixture; the overall volume was 25 mL. The optical density of the thus obtained solution was determined at $\lambda = 260$ nm (adsorption of the $HgBr_3^-$ complex). The concentration of $Hg(OAc)_2$ (the cell width was 1 cm) was calculated from Eq. (1), and the accuracy was better than 5 %.

$$D = 1.19 \cdot 10^4[\text{Hg(OAc)}_2] \qquad (1)$$

Kinetic experiments were carried out at 25±0.1° C until the degree of conversion of $Hg(OAc)_2$ was 65—80 %. The initial concentrations of reagents for mercuration of **1** were $(1.0\div3.0) \cdot 10^{-2}$ mol L^{-1}, $[\text{NaOAc}] = (0\div1.0) \cdot 10^{-4}$ mol L^{-1}. At higher concentrations of NaOAc, the reaction was carried out under pseudo-first order conditions using the following concentrations:

[NaOAc] /mol L^{-1}	$[\text{Hg(OAc)}_2]$ /mol L^{-1}	[Bornylene] /mol L^{-1}
$2.5 \cdot 10^{-4}$—$5.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-2}$—$7.0 \cdot 10^{-2}$
$(1.0$—$5.0) \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-2}$—$7.0 \cdot 10^{-2}$

The formation of complexes from $Hg(OAc)_2$ and NaOAc in MeOH was estimated by ^{199}Hg NMR spectra.* Variable amounts of NaOAc were added to a 0.1 *M* solution of $Hg(OAc)_2$ in methanol, and chemical shifts for ^{199}Hg (δ) were recorded. The results obtained are given below.

[NaOAc] /mol L^{-1}	0.05	0.10	0.15	0.20	0.30	0.40	0.50	1.00
$\Delta\delta$ ^{199}Hg	19.5	55.2	67.3	77.8	95.7	108.8	119.1	152.4

The complexation constant (*K*) was calculated from Eq. (2).[18]

$$\Delta\delta = 1/C\{[(C + C')(\delta_x - \delta_0)/2 + (\delta_x - \delta_0)/(2K)] - \qquad (2)$$

$$-\sqrt{[(C+C')(\delta_x-\delta_0)/2+(\delta_x-\delta_0)/(2K)]^2 - CC'(\delta_x-\delta_0)^2}\}$$

where $\Delta\delta$ is the observed relative change in δ ^{199}Hg, δ_x is the chemical shift of the complex relative to the chemical shift of a 0.1 *M* solution of $Hg(OAc)_2$ (δ_0), and C/mol L^{-1} and C'/mol L^{-1} are concentrations of $Hg(OAc)_2$ and NaOAc, respectively.

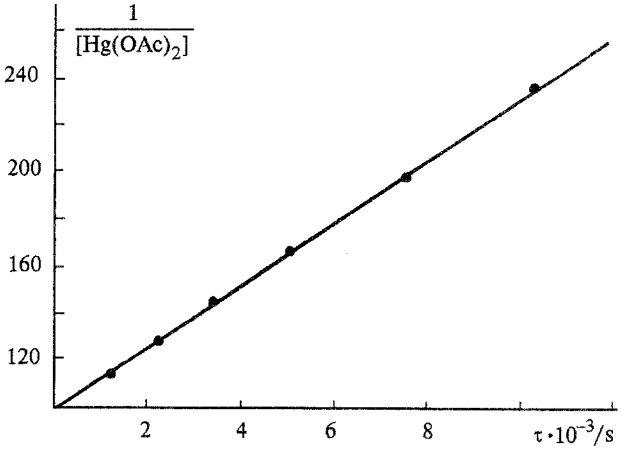

Fig. 1. Anamorphosis of Eq. (3) for the reaction of $Hg(OAc)_2$ with bornylene in MeOH: $[\text{Hg(OAc)}_2]_0 = [\text{Bornylene}]_0 = 0.01$ mol L^{-1}.

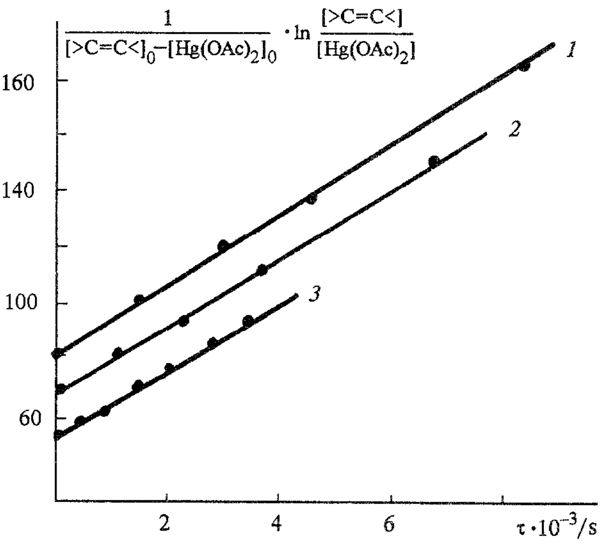

Fig. 2. Anamorphosis of Eq. (3) for the reaction of $Hg(OAc)_2$ with bornylene in MeOH:
1, $[\text{Hg(OAc)}_2]_0 = 0.01$ mol L^{-1}, $[\text{Bornylene}]_0 = 0.015$ mol L^{-1};
2, $[\text{Hg(OAc)}_2]_0 = 0.01$ mol L^{-1}, $[\text{Bornylene}]_0 = 0.02$ mol L^{-1};
3, $[\text{Hg(OAc)}_2]_0 = 0.01$ mol L^{-1}, $[\text{Bornylene}]_0 = 0.032$ mol L^{-1}.

All of the calculations were done using minimization of the sum of the squared deviations by the Nelder—Meed simplex-method.[19] The mean squar deviation of optimal *K* and ($\delta_x - \delta_0$) values was determined by the standard method using the response function linearized in the vicinity of the minimum point for the sum of the squared deviations.[20]

Results and Discussion

As can be seen from Figs. 1 and 2, interaction of $Hg(OAc)_2$ with **1** in methanol is described by a second-

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* Determination was carried out in collaboration with Dr. Yu. K. Grishin, M. V. Lomonosov Moscow State University.

Table 1. Rate constants for mercuration of bornylene with $Hg(OAc)_2$ determined experimentally and calculated from Eq. (10)

Solvent	[NaOAc] /mol L^{-1}	$k_{exp} \cdot 10^3$ /L mol^{-1} s^{-1}	$k_{calc} \cdot 10^3$ /L mol^{-1} s^{-1}
MeOH	–	11.48±0.51	
	$5.0 \cdot 10^{-5}$	8.02±0.49	5.69
	$1.0 \cdot 10^{-4}$	4.40±0.07	4.31
	$2.5 \cdot 10^{-4}$	2.48±0.12	2.65
	$5.0 \cdot 10^{-4}$	1.67±0.14	1.78
	$1.9 \cdot 10^{-3}$	1.30±0.08	1.24
	$1.5 \cdot 10^{-3}$	1.05±0.04	1.04
	$2.0 \cdot 10^{-3}$	0.92±0.03	0.93
	$3.0 \cdot 10^{-3}$	0.84±0.07	0.83
	$4.0 \cdot 10^{-3}$	0.79±0.06	0.77
	$5.0 \cdot 10^{-3}$	0.80±0.01	0.74
	$1.0 \cdot 10^{-2}$	0.72±0.02	0.67
	$2.0 \cdot 10^{-2}$	0.60±0.01	0.64
	$5.0 \cdot 10^{-2}$	0.55±0.01	0.62
EtOH	–	1.26±0.08	
	$5.0 \cdot 10^{-3}$	0.24±0.02	
Pr^nOH	–	0.65±0.02	
	$5.0 \cdot 10^{-3}$	0.28±0.02	
MeCOOH	–	54.40±1.12	
	0.1	37.45±2.11	

Table 2. Rate constants for mercuration of cyclohexene in methanol

Reagent	[NaOAc]/mol L^{-1}	k/L mol^{-1} s^{-1}
$Hg(OAc)_2$	–	1.23±0.07 (1.82)[17]
	0.002[a]	$(2.74 \pm 0.20) \cdot 10^{-2}$
	0.01[a]	$(1.43 \pm 0.08) \cdot 10^{-2}$
	0.015[a]	$(1.32 \pm 0.16) \cdot 10^{-2}$
$Hg(OAc)_2$—NaN_3[b] (1 : 3)	–	$(7.3 \pm 0.44) \cdot 10^{-5}$

[a] $[Hg(OAc)_2] = 2.0 \cdot 10^{-4}$ mol L^{-1}, $[C_6H_{10}] = 6.0 \cdot 10^{-3}$ mol L^{-1}. [b] $[Hg(OAc)_2] = 1.0 \cdot 10^{-3}$ mol L^{-1}, $[C_6H_{10}] = 0.1$ mol L^{-1}.

order equation (first order with respect to each reagent).

$$-d[Hg(OAc)_2]/dt = k[Hg(OAc)_2][>C=C<] \quad (3)$$

It was analogously shown that Eq. (3) is applicable to the interaction of $Hg(OAc)_2$ with **1** in ethanol and *n*-propanol. The same kinetic features were established for a series of other reactions of alkene solvo-mercuration.[17,21] The rate constants for mercuration of compounds **1** and **2** are given in Tables 1 and 2, respectively. The NaOAc additives dramatically slow down the reaction in alcohols, but the appearance of the kinetic equation is retained (Fig. 3, see Tables 1, 2). Thus, when [NaOAc] = $5.0 \cdot 10^{-3}$ mol L^{-1}, the rate of mercuration of **1** in methanol is 14.3 times lower, while for ethanol and propanol it is 5.2 and 2.3 times lower, respectively. In the case of mercuration of **1** in acetic acid, even the presence of 0.1 *M* NaOAc reduces the reaction rate insignificantly (see Table 1).

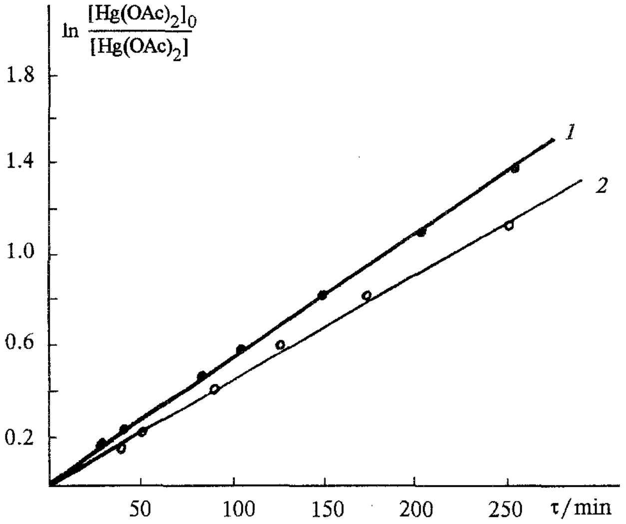


Fig. 3. Anamorphosis of Eq. (3) for the reaction of $Hg(OAc)_2$ with bornylene (*1*) and cyclohexene (*2*) in MeOH in the presence of NaOAc:
1, $[Hg(OAc)_2]_0 = 1.01 \cdot 10^{-3}$ mol L^{-1}, $[Bornylene]_0 = 5.46 \cdot 10^{-2}$ mol L^{-1}, $[NaOAc]_0 = 1.00 \cdot 10^{-3}$ mol L^{-1};
2, $[Hg(OAc)_2]_0 = 2.02 \cdot 10^{-4}$ mol L^{-1}, $[C_6H_{12}]_0 = 6.77 \cdot 10^{-3}$ mol L^{-1}, $[NaOAc]_0 = 0.01$ mol L^{-1}.

The introduction of $LiClO_4$ additives increases the reaction rate according to the normal salt effect equation[10,22] (Table 3)

$$k = k_0(1 + B[LiClO_4]), \quad (4)$$

where k_0 is the rate constant in the absence of salt, and $B = 23$.

NaOAc additives effectively influence the distribution of the products of mercuration of **1** (Fig. 4, Table 4). Thus, when [NaOAc] = 0.01 mol L^{-1}, the amount of solvo-adducts is sevenfold smaller, and when [NaOAc] = 0.05 mol L^{-1}, the formation of solvo-adducts is not observed. It should be pointed out that the change in the composition of products depending on the salt concentration is more monotonic than the change in the rate

Table 3. Rate constants for mercuration of bornylene with $Hg(OAc)_2$ in the presence of $LiClO_4$ in methanol

$[LiClO_4]$/mol L^{-1}	$k \cdot 10^2$/L mol^{-1} s^{-1}
0.01	1.40±0.06
0.05	2.84±0.09
0.1	3.82±0.09

Table 4. The effect of NaOAc concentration on the ratio between the adducts and the solvo-adducts ($[A_1]/[A_2]$)

$[NaOAc]/mol\ L^{-1}$	$[A_1]/[A_2]$
—	24 : 76
$5.0 \cdot 10^{-4}$	35 : 65
$1.0 \cdot 10^{-3}$	48 : 52
$1.5 \cdot 10^{-3}$	60 : 40
$2.0 \cdot 10^{-3}$	69 : 31
$2.5 \cdot 10^{-3}$	70 : 30
$3.0 \cdot 10^{-3}$	76 : 24
$3.5 \cdot 10^{-3}$	75 : 25
$4.0 \cdot 10^{-3}$	81 : 19

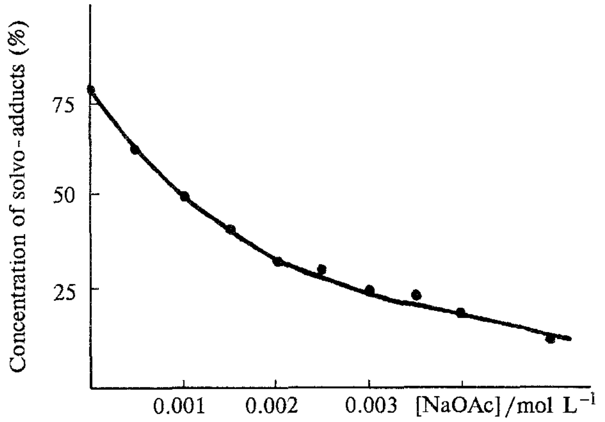


Fig. 4. Dependence of concentration of solvo-adducts on the concentration of NaOAc in the reaction of bornylene with $Hg(OAc)_2$ in MeOH.

constant. Thus, when $[NaOAc] = 5.0 \cdot 10^{-4}$ mol L^{-1}, the reaction in methanol exhibits a 6.9-fold decrease in the rate constant, while the amount of solvo-adducts is only 1.2 times less.

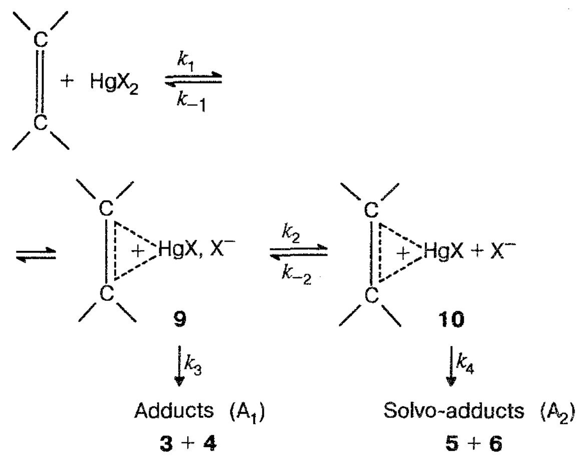
According to the literature data,[15] solvo-adduct **7** is the only product of the reaction of **2** with $Hg(OAc)_2$ in MeOH in the presence of NaOAc.

Comparison of the effect of NaOAc and $LiClO_4$ on the rate of mercuration of **1** indicates that the OAc^- ion has a retarding effect in general. It has been suggested more than once that in the case of NaOAc type salts this effect is caused by the complexation of the reagent.[6,17]

$$Hg(OAc)_2 + OAc^- \rightleftharpoons Hg(OAc)_3^-$$

To evaluate the influence of this factor on the mercuration rate we determined the equilibrium constant (*K*). The experimental value *K* = 4.6 shows that it is possible to neglect the effect of complexation on the reaction rate at the concentrations of $Hg(OAc)_2$ and NaOAc used. Thus, when $[Hg(OAc)_2] = [NaOAc] = 0.01$ mol L^{-1}, the equilibrium concentration of the complex is $4.2 \cdot 10^{-4}$ mol L^{-1}.

Scheme 1



When the data about the effect of NaOAc on the reaction rate and on the ratio between the products obtained in alcohols are analyzed, it is possible to conclude that the salt effect manifests itself through the common ion mechanism.[10] On these grounds, we believe that mercurinium intermediate (**9**), which is formed at the first stage of the reaction (Scheme 1), exists in equilibrium with solvated ion (**10**).

Intermediate **9** seems to be a close ion pair. This follows from the fact that, as the salt concentration increases, the reaction rate approaches a certain value, and the formation of adducts **3** and **4** becomes the main direction of the reaction of HgX_2 with **1**. Accordingly, at a certain limiting concentration of NaOAc, only ion pair **9** should participate in the reaction. In the reaction with compound **12**, this ion pair, as well as solvated ion **10**, converts to solvo-adduct **7**. In contrast, the reaction of ion pair **9** with compound **1** only affords adducts **3** and **4**. Presumably, if the salt concentrations are lower than the limiting concentration, ion pair **9** only converts to adducts **3** and **4** in the reaction with compound **1**, and ion **10** only transforms to solvo-adducts **5** and **6**.

With this in mind, and applying the steady-state concentration method to Scheme 1, Eq. (5) can be written as follows:

$$\frac{[A_1]}{[A_2]} = \frac{k_{-2}k_3[OAc^-]}{k_2 k_4} + \frac{k_3}{k_2} \qquad (5)$$

This equation attests that the ratio between the overall amount of adducts **3** and **4** (A_1) and the overall amount of solvo-adducts **5** and **6** (A_2) should be in a linear dependence on salt concentration (see Table 4), which is confirmed by the experimental data (Fig. 5). The linear dependence depicted in Fig. 5 can be represented by Eq. (6) (*r* = 0.985).

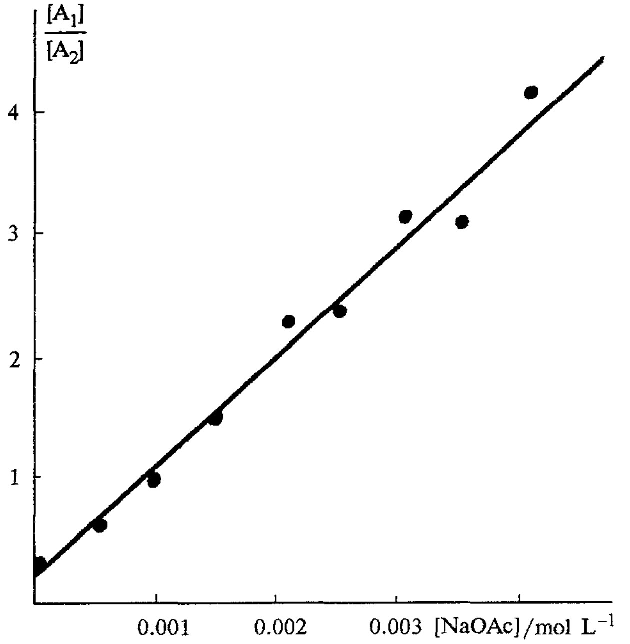


Fig. 5. Dependence of the $[A_1]/[A_2]$ ratio on the concentration of NaOAc.

$$\frac{[A_1]}{[A_2]} = (940 \pm 60)[OAc^-] + (1.14 \pm 0.15) \qquad (6)$$

The proposed mechanism of mercuration of alkenes is confirmed in the following way. When the concentration of NaOAc is lower than the limiting concentration, the application of the steady-state concentration method in accordance with Scheme 1 permits one to write

$$-\frac{d[Hg(OAc)_2]}{dt} = k_1\frac{k_3c + k_2k_4}{c(a - b)}[{>}C{=}C{<}][Hg(OAc)_2], \qquad (7)$$

where $a = k_{-1}+k_2+k_3$; $b = k_2k_{-2}[OAc^-]/(k_{-2}[OAc^-] + k_4)$; $c = k_{-2}[OAc^-] + k_4$.

After a series of transformations of this equation (see *Supplements*), expression (8) for the reaction rate is obtained.

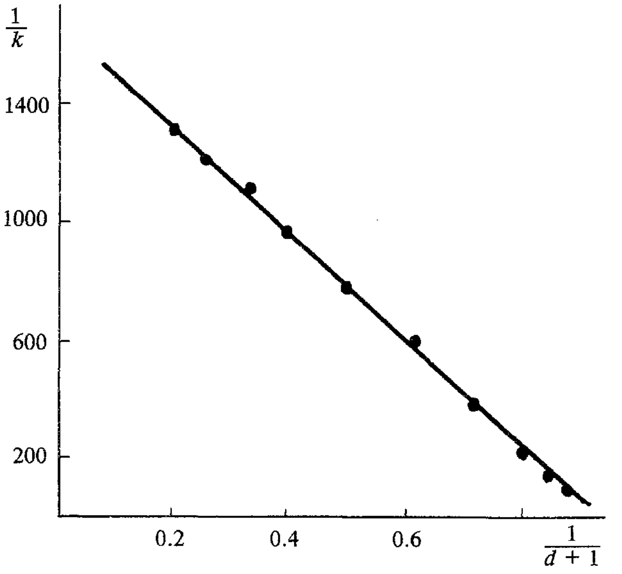


Fig. 6. Dependence of $1/k$ on the value of $1/(d+1)$ in the reaction of bornylene with $Hg(OAc)_2$ in methanol.

The expression for the reciprocal parameter $1/k$ is

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}}{k_3k_1} - \frac{k_{-1}}{k_3k_1}\cdot\frac{1}{k_{-2}k_3/(k_2k_4)\cdot[OAc^-] + k_3/k_2 + 1}, \qquad (9)$$

where the expression $d = k_{-2}k_3[OAc^-]/(k_2k_4) + k_3/k_2$ is equal to the right side of Eqs. (5) and (6).

Thus, the values of $1/k$ should depend linearly on $1/(d + 1)$ or $1/(940[OAc^-] + 1.14)$.

Figure 6 shows that Eq. (9) does satisfactorily describe the experimental data. The regression equation that approximates the graphic dependence depicted in Fig. 6 is expressed as

$$1/k = (1650 \pm 25) - (1750 \pm 44)/(940[OAc^-] + 1.14). \qquad (10)$$

Comparison of the values of k_{calc} calculated from Eq. (10) and the experimental values of k_{exp} reveals that they are reasonably close (see Table 1).

$$k_{eff} = \frac{k_1\left(\frac{k_3k_{-2}}{k_2k_4}\left[OAc^-\right] + \frac{k_3}{k_2} + 1\right)}{\left(\frac{k_{-2}k_3}{k_2k_4}\left[OAc^-\right] + \frac{k_3}{k_2} + 1\right) + \frac{k_{-1}}{k_3}\left(\frac{k_{-2}k_3}{k_2k_4}\left[OAc^-\right] + \frac{k_3}{k_2} + 1\right) - \frac{k_{-1}}{k_3}}, \qquad (8)$$

where k_{eff} is the reaction rate constant.

For limiting concentrations of NaOAc, when the stage of conversion of ion pair **9** into solvated ion **10** is absent, *i.e.*, $k_2 = 0$, it is possible to use Eq. (8) or, directly, the steady-state concentration method to establish the expression for the reaction rate constant k_∞:

$$k_\infty = k_1k_3/(k_{-1} + k_3) \qquad (11)$$

or

$$\frac{1}{k_\infty} = \frac{k_{-1}}{k_1k_3} + \frac{1}{k_1}\,. \qquad (12)$$

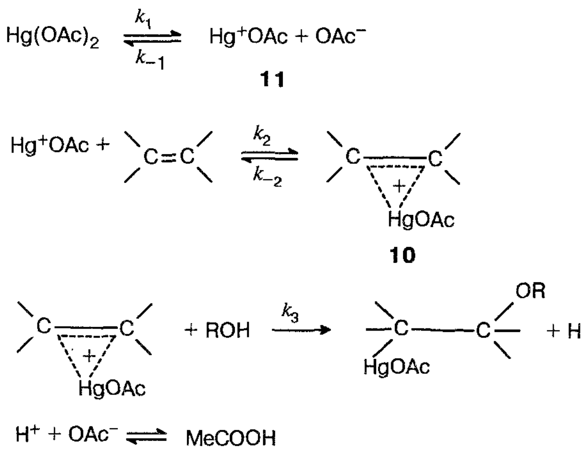
Equations (9), (10), and (12) attest that the segment, which is cut off at the ordinate axis (see Fig. 6), corresponds to $1/k_\infty = 1650$, and therefore $k_\infty = 6.0 \cdot 10^{-4}$ L mol^{-1} s^{-1}. The value of k_∞ calculated in this way is close to the experimental one ($5.97 \cdot 10^{-4}$ and $5.48 \cdot 10^{-4}$ L mol^{-1} s^{-1}, respectively).

Therefore, the detailed analysis of the proposed scheme for the mercuration of alkenes revealed that it agrees well with the kinetic data.

As the polar properties of the solvent decrease, the occurrence of the reaction through a solvated ion decreases (MeOH < EtOH < Pr^{n}OH). Unlike mercuration in alcohols, in acetic acid mercuration, apparently, only occurs with the participation of ion pair **9**. This conclusion agrees with the results of investigations of solvolytic transformations and addition reactions of sulfur-containing reagents to alkenes in acetic acid. It has been shown[22–24] that, in this solvent, various ion pairs, not free ions, participate in heterolytic reactions.

Now we want to consider an alternative scheme proposed by several authors[6,12] for the reaction of mercuric acetate with alkenes in alcohols (Scheme 2).

Scheme 2



In this case, the salt effect can manifest itself due to a shift in the first equilibrium in the direction of undissociated Hg(OAc)$_2$. Unfortunately, literature data about the degree of dissociation of Hg(OAc)$_2$ in alcohols, which would allow one to estimate the feasibility of this scheme, are lacking. Therefore, we must verify the correspondence between Scheme 2 and the experimental data by kinetic analysis.

If ions **10** and **11** obey the steady-state concentration principle, Eq. (13) is obtained.

$$\frac{d[\mathrm{Hg(OAc)_2}]}{dt} = \frac{k_1k_2k_3[\mathrm{Hg(OAc)_2}][{>}C{=}C{<}]}{k_2k_3[{>}C{=}C{<}] + (k_2k_{-1} + k_3k_{-1})[\mathrm{OAc^-}]} \qquad (13)$$

This equation shows that, if Scheme 2 is realized, the order with respect to olefin can vary from zero to unity depending on the ratio between the values in the denominator. Let us consider the case of $(k_{-2}k_1 + k_3k_{-1})[\mathrm{OAc^-}] \gg k_2k_3[{>}C{=}C{<}]$ in more detail, because under these conditions the order with respect to alkene and to the reagent coincide with the experimental data.

$$-\frac{d[\mathrm{Hg(OAc)_2}]}{dt} = \frac{k_1k_2k_3}{f[\mathrm{OAc^-}]}[\mathrm{Hg(OAc)_2}][{>}C{=}C{<}], \qquad (14)$$

where $f = k_2k_{-1} + k_3k_{-1}$.

Scheme 2 demonstrates that the concentration of OAc$^-$ during the reaction cannot exceed the value determined by the dissociation constant of MeCOOH in methanol ($2.0 \cdot 10^{-10}$)[25]. Therefore, when mercuration is carried out in the presence of NaOAc, the [OAc$^-$] value should be determined by the concentration of the added salt. In this case, Eq. (14) supports the conclusion that the effective rate constant should depend linearly on [OAc$^-$]$^{-1}$. Figure 7 shows that the expected dependence is not realized. Thus, Scheme 2 must be described by the general equation (13), which differs from the empirically found equation and attests to the incompatibility of Scheme 2 with the experimental data. In addition, if Scheme 2 is realized, regardless of the alkene structure a solvo-adduct would be the product of the reaction, because in this case counter-ion OAc$^-$ is an external nucleophile, which accounts for its very low concentration. Nevertheless, when the reaction of Hg(OAc)$_2$ with **1** is carried out in methanol in the absence of NaOAc, the molar proportion of adducts **3** and **4** amounts to 0.24, and in the case of ethanol and *n*-propanol, it is 0.6 and 0.9, respectively.[1] When carrying out the mercuration in MeOH even small additives of NaOAc (0.001 mol L^{-1}) result in the twofold increase of the content of products **3** and **4** (see Table 4). Analogous features were also observed for the interaction of Hg(OAc)$_2$ with norbornene[2] and bicyclo[2.2.2]octene.[2] So active competition in trapping the free mercurinium ion between such a weak nucleophile as the acetate ion and the solvent is virtually impossible.[26] Therefore, during formation of adducts **3** and **4**, OAc$^-$ is included in an intermediate, which is in contradiction with Scheme 2.

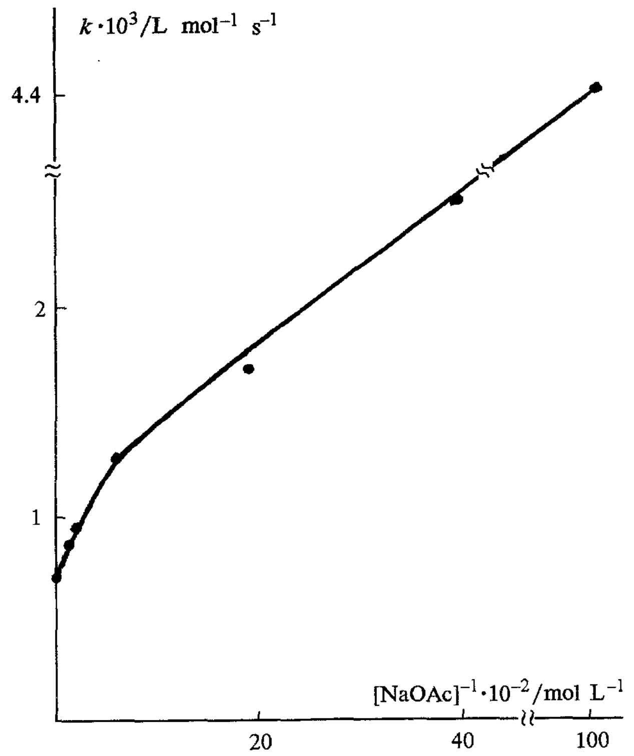


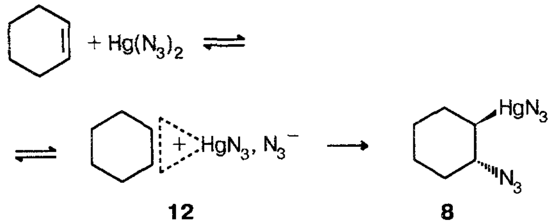
Fig. 7. Dependence of k on $[NaOAc]^{-1}$ in the reaction of bornylene with $Hg(OAc)_2$ in methanol.

Thus, the above-mentioned arguments and satisfactory correspondence between Scheme 1 and the experimental data point to the fact that in the reactions of $Hg(OAc)_2$ with alkenes in MeOH the main reagent is the salt itself, not free ion **11** (see Scheme 2). In ethanol, propanol, and in methanol in the presence of NaOAc additives, the parallel process according to Scheme 2 seems to be completely negligible.

It has been pointed out that in the reaction with cyclohexene, ion pair **9**, as well as the solvated ion, converts to solvo-adduct **7**. Probably, this is accounted for by a significant solvation effect that accompanies the formation of the ion pair. It is also possible that, at the limiting stage of the process characterized by the k_1 rate constant, the solvent exhibits the effect of nucleophilic participation.[27] The strongly solvated cation of ion pair **9** can react faster with the solvent than with the counter-ion OAc^-. When the nucleophilicity of the counter-ion increases, the formation of adducts should also be possible in the reaction with compound **2**. The data about azidomercuration of **2** with a $Hg(OAc)_2$—NaN_3 (1 : 3) system in MeOH are of significant interest. Earlier[3] we found that under these conditions the only product is *trans*-azidoadduct (**8**).

In the present work, the kinetic investigation carried out under conditions of an excess of reagent **2** revealed that this process obeys the laws of a pseudo-first-order reaction (see Table 2). Apparently, azidomercuration of **2**, like in acetic acid, proceeds *via* ion pair (**12**) as an intermediate, which reacts with counter-ion N_3^- faster than it transforms to the solvated mercurinium ion (Scheme 3).

Scheme 3



The presence of the solvated ion **10** in the reaction solution accounts for the fact that the reaction of mercury salts with alkenes proceeds as conjugated solvomercuration in lower alcohols and water-organic media. This is caused by the ease of the transformation (in such media) of the initially formed intermediate into a solvated ion, which further converts to solvo-adducts.

The results of our investigation refute the concerted mechanism of the formation of adducts and solvo-adducts in the reactions of bornylene and cyclohexene with mercuric acetate, which is also confirmed by the regiochemical data.[1] The important consequence of the participation of polar species in the reaction is the fact that the mercurinium intermediates are able to convert not only to *trans*-, but also to *cis*-adducts, which is possibly due to the frontal attack of the nucleophile on them.

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Supplements

According to Scheme 1, the ovelall reaction rate is

$$-\mathrm{d}[\mathrm{Hg(OAc)_2}]/\mathrm{d}t = \mathrm{d}[\mathrm{A_1}]/\mathrm{dt} + \mathrm{d}[\mathrm{A_2}]/\mathrm{d}t. \tag{I}$$

Using the steady-state concentration method, we obtain

$$\frac{\mathrm{d}[\mathrm{A_1}]}{\mathrm{d}t} = \frac{k_1k_3[\mathrm{>C{=}C<}][\mathrm{Hg(OAc)_2}]}{k_{-1} + k_2 + k_3 - k_2k_{-2}\left[\mathrm{OAc^-}\right]/(k_{-2}\left[\mathrm{OAc^-}\right] + k_4)} \tag{II}$$

and

$$\frac{\mathrm{d}[\mathrm{A_2}]}{\mathrm{d}t} = \frac{k_1k_2k_4[\mathrm{>C{=}C<}][\mathrm{Hg(OAc)_2}]}{\{k_{-1} + k_2 + k_3 - k_2k_{-2}\left[\mathrm{OAc^-}\right]/(k_{-2}\left[\mathrm{OAc^-}\right] + k_4)\}\cdot(k_{-2}\left[\mathrm{OAc^-}\right] + k_4)} \tag{III}$$

Equations (I)—(III) make it possible to obtain

$$k = \frac{k_1(k_3k_{-2}\left[\mathrm{OAc^-}\right] + k_3k_4 + k_2k_4)}{k_{-2}\left[\mathrm{OAc^-}\right](k_{-1} + k_3) + k_4(k_{-1} + k_3) + k_2k_4} \tag{IV}$$

Division of the numerator and denominator of Eq. (IV) by k_2k_4 results in

$$k = \frac{k_1\{k_3k_{-2}\left[\mathrm{OAc^-}\right]/(k_2k_4) + k_3/k_2 + 1\}}{k_{-2}\left[\mathrm{OAc^-}\right](k_{-1} + k_3)/(k_2k_4) + (k_{-1} + k_3)/k_2 + 1} \tag{V}$$

Transformation of the denominator in Eq. (V) gives

$$\frac{k_{-1}k_{-2}\left[\mathrm{OAc^-}\right]}{k_2k_4} + \frac{k_{-2}k_3\left[\mathrm{OAc^-}\right]}{k_2k_4} + \frac{k_{-1}}{k_2} + \frac{k_3}{k_2} + 1$$

or

$$\left(\frac{k_{-2}k_3\left[\mathrm{OAc}^-\right]}{k_2k_4} + \frac{k_3}{k_2} + 1\right) + k_{-1}\left(\frac{k_{-2}\left[\mathrm{OAc}^-\right]}{k_2k_4} + \frac{1}{k_2}\right) \qquad \text{(VI)}$$

After transformation of the second item inside the brackets (addition and subtraction of 1, then multiplication and decision by k_3), expression (VI) converts to the following one:

$$\left(\frac{k_{-2}k_3\left[\mathrm{OAc}^-\right]}{k_2k_4} + \frac{k_3}{k_2} + 1\right) + \frac{k_{-1}}{k_3}\left(\frac{k_{-2}k_3\left[\mathrm{OAc}^-\right]}{k_2k_4} + \frac{k_3}{k_2} + 1 - 1\right) \qquad \text{(VII)}$$

Replacing the denominator in Eq. (V) with expression (VII) gives the expression for the rate constant (see Eq. (8)).