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KINETICS OF THE VINYL INTERCHANGE REACTION BETWEEN BENZOIC ACID AND VINYL ACETATE

G. SLINCKX and G. SMETS
Laboratoire de Chimie Macromoléculaire, Université de Louvain, Belgique

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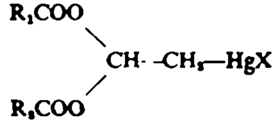
Abstract—In this paper, the kinetics of the vinyl interchange reaction between benzoic acid and vinyl acetate are reported. The mixed catalyst used was mercuric acetate dissolved in BF_3-acetic acid complex, the reaction being followed by IR spectrometry in a large excess of vinyl acetate at 30°. The reaction is first order with respect to the concentrations of BF_3-acetic acid and of mercuric salt. At constant HgO/BF_3 ratio (about unity) the overall order of reaction is two when the concentrations of mercury salt and BF_3 are varied simultaneously. With respect to the benzoic acid concentration, the reaction order tends to unity when the acid concentration is low. This effect was interpreted on the basis of the association of the carboxylic acid in the medium and demonstrated by a measure of the partition coefficients. With ethyl acetate as a solvent, a linear relation between vinyl acetate concentration and reaction rate is found; the activation energy was 9·4 Kcal/mole.

The importance and the nature of side reactions, especially the formation of ethylidene diesters and their influence on the equilibrium position, were examined. The kinetic results are in good agreement with the mechanism discussed in the previous paper.

Résumé—La réaction d'échange vinylique entre l'acide benzoïque et l'acétate de vinyle a été étudiée cinétiquement à 30° dans l'acétate de vinyle en excès et en présence d'un catalyseur à base d'acétate mercurique et d'acide acétotrifluoroborique. Le degré d'avancement de la réaction a été suivi par spectrométrie infra-rouge. La réaction est du premier ordre par rapport aux concentrations en acide trifluoroborique et en sel mercurique. A rapport HgO/BF_3 constant et voisin de l'unité, l'ordre global de la réaction est égal à deux si on fait varier les concentrations de l'oxyde de mercure et du trifluorure de bore simultanément. L'ordre de réaction par rapport à la concentration en acide benzoïque tend vers l'unité lorsque cette concentration est faible. Cet effet est interprété sur la base d'une association de l'acide carboxylique, dans le milieu, ce qui a été démontré par des mesures de coefficient de partage. Dans l'acétate d'éthyle comme solvant, la vitesse de réaction est proportionnelle à la concentration en ester vinylique. L'énergie d'activation de la réaction s'élève à 9·4 Kcal/mole.

L'importance et la nature des réactions secondaires, principalement les réactions de formation de diesters d'éthylidène, ont été examinées. Les résultats cinétiques sont en bon accord avec le mécanisme décrit dans la publication précédente.

IN THE previous paper,[1] the mechanism of vinyl interchange between a carboxylic acid and vinyl acetate was investigated by means of PMR spectroscopy. It was shown that the mechanism involves the formation of a transitory complex of the type:



$$\begin{matrix} R_1COO & \\ & \diagdown \\ & CH\text{—}CH_2\text{—}HgX \\ & \diagup \\ R_2COO & \end{matrix}$$

where X is an aryloxy or an acyloxy group.

The kinetics of this vinyl interchange reaction does not appear to have been investigated and in present paper, the detailed reaction mechanism in the case of benzoic acid–vinyl acetate has been examined.

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[1] G. Slinckx and G. Smets, *Tetrahedron*

EXPERIMENTAL

Acetic acid was purified by the method of Orton and Bradfield.[2] It was heated with 2–4% CrO_3 and freshly distilled; its water content being determined cryoscopically, a lowering of m.p. of 0·2° corresponding to 0·1% water. The calculated amount of Ac_2O was then added in the presence of a few drops of H_2SO_4. After careful rectification it melted at 16·6°.

Benzoic acid was an analytical grade U.C.B. product.

Vinyl acetate pure monomer was dried on $CaCl_2$ and carefully rectified (b.p. 72°) with a Widmer column of 50 cm length.

Boron fluoride-acetic acid complex. BF_3 was obtained following the procedure of Gasselin[3] and purified by the method of Booth and Willson;[4] it was absorbed in anhyd AcOH. A soln of the complex was titrated potentiometrically in Ac_2O–AcOH (2·1) medium with a standard AcOK soln in anhyd AcOH, between a glass electrode and a Beckman calomel electrode No. 1190. A sat. LiCl soln in AcOH was used instead of the usual KCl bridge. The titration was carried out in a closed vessel under a stream of pure N. The AcOK soln was titrated with a H_2SO_4 soln in AcOH in the presence of methylviolet as indicator. In this medium H_2SO_4 behaves as a monobasic acid; a typical titration curve is reproduced in Fig. 1.

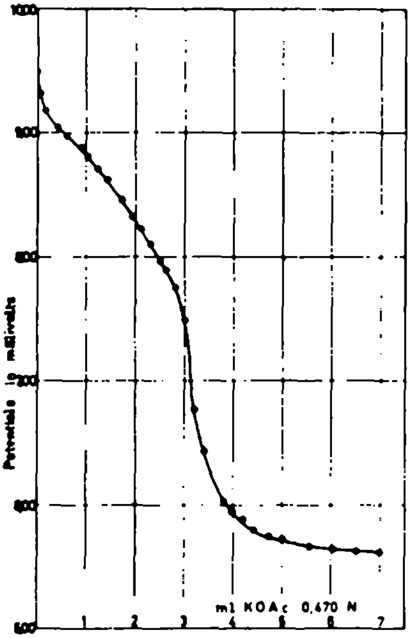

Fig. 1. Potentiometric titration of ($HOAc$–BF_3) complex with potassium acetate. Solvent: acetic anhydride–acetic acid.

Preparation "in situ" *of the mercuri fluoroboroacetate catalyst.* A given amount of HgO was dissolved in anhyd AcOH. This soln was quantitatively added to the reagents. When the desired volume of strong acid BF_3–HOAc was added, the reaction started instantaneously. The catalyst (mercuric acetate + strong acid) was never prepared separately on account of the precipitation of a complex mercury compound and the lack of reproducibility of measurements in this case. The use of fluoroboroacetic acid instead of H_2SO_4 had the advantage of decreasing the extent of secondary reactions. For experiments using different concentrations of mercuric oxide, the oxide was always dissolved in a constant volume of anhyd AcOH; similarly the volume of acetic catalyst soln was kept

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[2] K. J. Orton and A. E. Bradfield, *J. Chem. Soc.* **125**, 960 (1924); 983 (1927).

[3] M. V. Gasselin, *Ann. Chim. Phys.* (7) 3, 5 (1894).

[4] H. S. Booth and K. S. Willson, *Inorganic Synthesis* p. 21. Wiley, N.Y. (1939).

constant. For experiments using different BF_3 concentrations, the total volume of AcOH i.e. the total volume used as solvent for the BF_3, and HgO was also kept constant.

Vinyl interchange reaction

Analytical methods. The reaction was carried out in a 3-necked flask provided with a drying tube, a Hg valve-stirrer and a sampling device by which a given volume (5 or 10 ml) of soln could be withdrawn. The degree of conversion was measured spectrometrically.

The sample was collected in a 25 ml graduated flask, mixed with 0·2 ml sat. AcOK soln in AcOH (in order to stop the reaction), and diluted up to 25 ml with pure cyclohexane (pure for chromatography). From this soln, 5 ml were taken off, and neutralized by shaking with 25 ml ice-cold 0·2N NaOH (sat. with NaCl) in order to remove the unreacted BzOH as well as AcOH. After separation the organic layer, was dried over $CaCl_2$ and examined by IR spectrometry (Perkin–Elmer 21 double beam spectrometer, cell thickness of 0·05 or 0·1 mm). The analytical band used for determining the degree of conversion was that of vinyl benzoate at 706-707 cm^{-1} ($\varepsilon_{VB} = 42{\cdot}8\ cm^2/mole$). Taking into account that vinyl acetate absorbs in the same region (703 cm^{-1}), although its extinction coefficient is much lower ($\varepsilon_{VB} = 0{\cdot}444\ cm^2/mole$), its presence in a large excess makes it necessary to establish a calibration curve, by plotting the total measured optical density as a function of a vinyl benzoate concentration. In such a diagram the intercept on the ordinates represents the nearly constant contribution of vinyl acetate to the total absorption in the experimental conditions.

In the absence of a secondary reaction, the total acid concentration (BzOH and AcOH) of the reaction medium must remain constant. The formation of ethylidene diesters corresponds to a decrease in acid content of the system and it is obvious that the molar concentration of diester is equal to the decrease in molar acid concentration. Therefore, the ethylidene compound formed was evaluated by acid titration in non-aqueous medium with MeOK: a 2 ml sample of the soln was diluted with a 3:1 mixture of anhyd benzene–MeOH and titrated in the presence of thymol blue as indicator with 0·2N MeOK in the same benzene–MeOH mixed solvent. Only initial rates were used for determining the reaction kinetics on account of the existence of the reverse equilibrium reaction and the changing order with respect to the acid concentration. They were evaluated graphically from the initial slope of the corresponding concentration/time curves.

Interchange kinetics

In order to control the proposed reaction mechanism between vinyl acetate and BzOH, the rate dependency on the reagent concentrations and catalyst composition was examined successively.

1. *Influence of the mercuric salt and borontrifluoride concentration.* No interchange reaction takes place at the usual temp, even after 2 months, in the absence either of Hg compound or strong acid; both components must be present simultaneously in order to catalyse the interchange process. In the absence of Hg salt some ethylidene diester is formed due to the acid catalysis, but the interchange reaction does not occur.

Two series A and B of experiments were carried out—in each only the initial Hg salt concentration varied. The experimental conditions and results are summarized in Table 1 (A and B); the reaction order was determined with respect to the vinyl acetate concentration, this reagent being used at the same time as solvent.

For illustration, the rate curves of series A are represented in Fig. 2. The corresponding initial rates obey a first-order reaction mechanism with respect to the HgO concentration; by plotting the rate versus the HgO concentration linear diagrams passing through the origin were obtained (Fig. 3 A and B).

In the experiments of series C (Table 1), the concentration of BF_3 was varied, the other concentrations being kept constant. Here again, the initial rates are directly proportional to the BF_3 concentration, and the diagram passes through the origin (Fig. 3c) i.e. Hg salts are inactive in the absence of strong acid.

2. *Influence of the catalytic complex concentration.* In order to determine the mode of action of the strong acid with Hg salt as well the mode of action of the resulting compound on the reaction course, two new series D and E of experiments were carried out at constant ratio of both components but at different molar concentrations (Table 2).

Taking into account that in each series the ratio HgO:BF_3 was constant, it is evident that the slope of a logarithmic plot of the rate against the BF_3 concentration indicates the sum of the orders

TABLE 1. RATE OF TRANSVINYLATION. INFLUENCE OF THE CONCENTRATIONS OF MERCURIC SALT AND BORON FLUORIDE AT T = 30°

Series A (BzOH) = 0·9615 mole l^{-1} (AcOV) = 9·615 mole l^{-1}
(AcOH) = 0·168 mole l^{-1} (BF_3) = 5·558 . 10^{-3} mole l^{-1}

HgO mole l^{-1} 10^3	Initial rate mole l^{-1} sec^{-1} 10^4	HgO/BF_3 ratio
(a) 0·8129	0·38	0·1463
(b) 1·3548	0·76	0·2437
(c) 2·7096	1·28	0·4875
(d) 5·4192	2·78	0·9750

Series B (BzOH) = 0·5095 mole l^{-1} (AcOV) = 10·19 mole l^{-1}
(AcOH) = 0·178 mole l^{-1} (BF_3) = 2·833 . 10^{-3} mole l^{-1}

(a) 1·441	0·42	0·509
(b) 2·130	0·66	0·747
(c) 2·872	0·87	1·014
(d) 3·574	0·97	1·262
(e) 3·594	1·04	1·270

Series C (BzOH) = 0·9615 mole l^{-1} (AcOV) = 9·615 mole l^{-1}
(AcOH) = 0·168 mole l^{-1} (HgO) = 2·7098 . 10^{-3} mole l^{-1}

BF_3 mole l^{-1} 10^3	Initial rate mole l^{-1} sec^{-1} 10^4	HgO/BF_3 ratio
(a) 1·112	0·43	2·436
(b) 1·667	0·69	1·625
(b') 1·667	0·70	1·625
(c) 2·779	1·07	0·975
(d) 4·168	1·67	0·650

by which each BF_3 and Hg salt participate in the interchange (Fig. 4). Indeed, this slope was found to be equal to 2 for series D, as expected from the rate dependence of BF_3 and Hg salt concentrations separately. Only at high Hg salt concentration does the slope decrease. In the series E, where the concentration ratio HgO:BF_3 as well as the Hg salt concentration are relatively high, the apparent overall order drops to about 1·4.

3. *Influence of the benzoic acid and vinyl acetate concentration.* By limiting the measurements to a small degree of conversion, the rate of interchange was studied as a function of the BzOH concentration. The data are summarized in Table 3. By plotting in a logarithmic diagram the initial rate versus the BzOH concentration, a decreasing apparent order of reaction with increasing acid concentration has been found (Table 3); this effect results mainly from the association of BzOH in the reaction medium, assuming that the monomeric acid is the only active species for the interchange. Indeed, the partition coefficient *K* of benzoic acid at 30° between water and vinyl acetate has been evaluated from titrations of the BzOH in aqueous phase after extraction with water of solutions of different concentrations in vinyl acetate; a mean value of 1·56 was found, i.e. mainly monomeric and associated, likely dimeric, molecules of BzOH are present in the reaction medium. Of course this figure will probably change when the reaction proceeds and the concentration of AcOH increases. An increasing concentration of BzOH may also effect the nature of the anion bonded to the Hg ion. But in any case this result corroborates, at least qualitatively, the interpretation for a changing apparent order of reaction with respect to the acid concentration; this order becomes unity only in diluted systems.

The study of the rate dependence from the vinyl acetate concentration necessitates the use of a solvant inert in the vinyl interchange reaction conditions, and structurally similar to the vinyl ester;

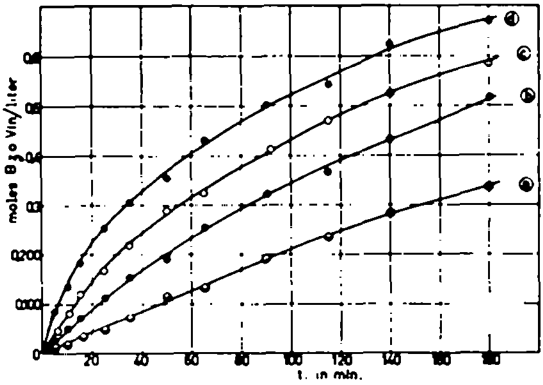


FIG. 2. Rate of vinyl benzoate formation. Dependency on the mercuric salt concentration. Table 1: series A.

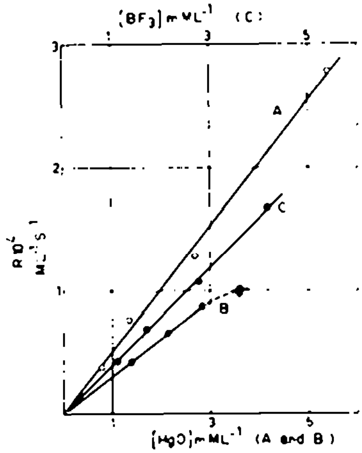


FIG. 3. Rate dependence on the boron trifluoride (curve C) and mercury–oxide concentrations (curves A and B).

TABLE 2. RATE OF TRANSVINYLATION. INFLUENCE OF THE CONCENTRATION OF CATALYTIC COMPLEX, $Hg(OAc)_2{\cdot}BF_3(HOAc)_2$

(BzOH) = 0·5095 M l^{-1} (AcOV) = 10·19 M l^{-1}
(AcOH) = 0·178 M l^{-1} T = 30·4°

Series D: HgO/BF_3 = 1·203		Series E: HgO/BF_3 = 1·3755	
BF_3 mole l^{-1} . 10^3	Initial rate mole l^{-1} sec^{-1} . 10^4	BF_3 mole l^{-1} . 10^3	Initial rate mole l^{-1} sec^{-1} . 10^4
0·5962	0·09	1·043	—
0·8435	0·18	1·252	0·306
1·005	0·27	1·565	0·385
1·1925	0·37	2·087	1·624
1·5	0·54	2·608	0·846
2·385	0·92	3·130	1·010

it should also present a high optical transmittance in the IR spectral region used for the quantitative determination. Since these requirements are practically fullfilled by AcOEt, it was selected as diluent in the experiments of Table 4.

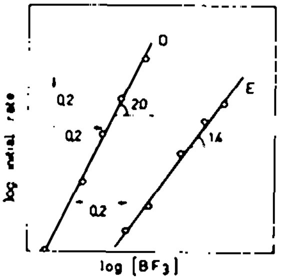


Fig. 4. Rate dependence of the boron trifluoride concentration at constant HgO:BF$_3$ ratio — $(=f)$
curve D $f = 1{\cdot}203$
curve E $f = 1{\cdot}3755$

The corresponding curves, conversion *vs.* time, revealed an inhibition period, the length of which increases with a decrease of initial vinyl ester concentration (Fig. 5). Interactions between AcOEt and the strong acid (BF$_3$–AcOH) are responsible for a decrease of free strong acid and retard the formation *in situ* of the catalytic complex. After the initial inhibition period the shape of the curves are entirely normal; therefore, the conversion curves were prolonged down to zero time (dotted lines) and the initial rates evaluated, neglecting the inhibition period. Although these results with AcOEt are not very significant, on account of the inhibition period which makes the evaluation of

TABLE 3. RATE OF TRANSVINYLATION. INFLUENCE OF BENZOIC ACID CONCENTRATION.

(AcOV) = 9·615 M l^{-1} (HgO) = 2·871 . 10^{-3} M l^{-1}
(AcOH) = 0·168 M l^{-1} (BF$_3$) = 2·915 . 10^{-3} M l^{-1}
T = 30·4°

BzOH mole l^{-1}	Initial rate mole l^{-1} sec^{-1} . 10^4	n apparent order
0·307	0·50	0·99
0·5095	0·76	0·67
0·713	0·93	0·57
0·840	1·0	0·45
0·9615	1·07	0·33

TABLE 4. RATE OF TRANSVINYLATION. INFLUENCE OF VINYL ACETATE CONCENTRATION.

solvent: EtOAc T = 30°
(BzOH) = 0·925 M l^{-1} (HOAc) = 0·259 M l^{-1}
(HgO) = 2·606 mM l^{-1} (BF$_3$) = 5·346 mM l^{-1}

AcOV mole l^{-1}	AcOEt mole l^{-1}	Initial rate mole l^{-1} sec^{-1} . 10^4
0·555	9·57	0·56
1·11	8·61	1·14
1·85	8·09	1·9
2·59	7·39	3·3

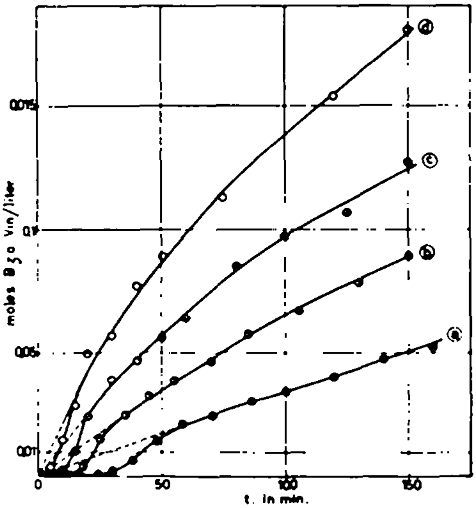


FIG. 5. Rate of vinyl interchange. Influence of vinyl acetate concentration.

the initial rates inaccurate, a direct proportionality between rate and vinyl ester concentration can be assumed.

4. *Activation energy of the interchange reaction.* Rate measurements were carried out at 20, 30 40 and 50°. Previously the importance of side reactions at these different temps were evaluated, but as far as the initial period only is concerned these side reactions may be neglected from kinetics points of view. As the reaction proceeds, they become detectable (at 40°) and quite observable at 50°. The data are given in Table 5.

TABLE 5. VINYL INTERCHANGE REACTION. INFLUENCE OF THE TEMPERATURE.

(BzOH) = 0·5095 M l^{-1} (AcOV) = 10·19 M l^{-1}
(HgO) = 2·871 mM l^{-1} (BF_3) = 2·934 mM l^{-1}

T	Initial rates mole l^{-1} sec^{-1} . 10^4
20	0·41
30	0·74
40	1·1
50	2·0

An Arrhenius plot of log (rate) *vs.* $1/T$ gives an activative energy of only 9·4 Kcal/mole, a value that is quite low when compared with the usual transesterifications or esterification reactions. This great difference is evidently directly related to the reaction mechanism and the specific role of the Hg compound in the vinyl interchange. It has not been possible to evaluate the activation energy of the reverse reaction, i.e. the vinyl interchange between vinyl benzoate and acetic acid. Due to the high benzoate concentration, the accuracy of the determination is insufficient; moreover side reactions interfere strongly.

5. *Influence of the temperature on the equilibrium.* In order to determine the yield of the vinyl interchange reaction between vinyl acetate and benzoic acid, and, if possible, the reaction enthalpy, some reactions were followed at different temps over a longer period of time. The corresponding conversion *vs.* time curves (Fig. 6) show clearly the occurrence of side reactions, especially at higher temps, where the curve passes through a maximum. The values on the ordinates are inaccurate on account of interference in the IR absorption by the ethylidene diester; moreover after some time, a partial, or even a complete, deactivation of the catalyst occurs with precipitation of metallic Hg. The occurrence of side reactions even at 30° was also shown by two experiments carried out in

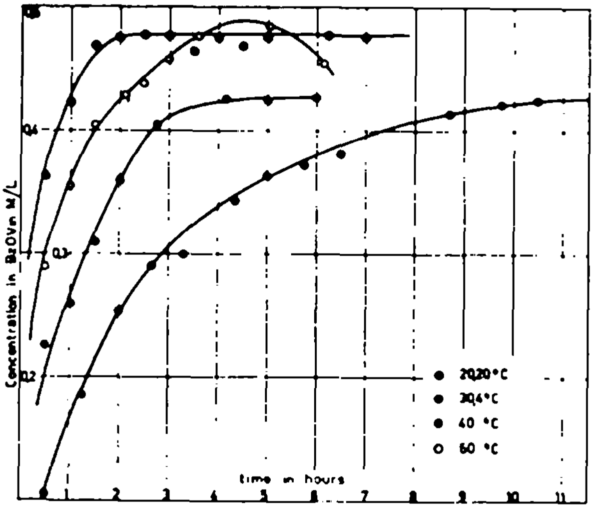


Fig. 6. Vinyl interchange reaction at different temperatures

(BzOH) = 0·5095 M l^{-1} (AcOV) = 10·19 M l^{-1}
(AcOH) = 0·178 M l^{-1} (HgO): 5·316 mM l^{-1}
(BF_3): 3·548 mM l^{-1}

AcOEt as a solvent, one in the direct sense (benzoic acid, vinyl acetate), the other in the reverse sense (acetic acid, vinyl benzoate). As can be seen in Fig. 7, both curves tend apparently to the same equilibrium position; however after some time the vinyl benzoate concentration decreases progressively in both systems.

After reaction, the reaction products were isolated and analysed by IR spectrometry; the presence of ethylidene diacetate (bands at 1010, 1215, 1375 and 1765 cm^{-1}) and of ethylidene aceto-benzoate (bands at 835, 1010, 1375 and 1690 cm^{-1}) was demonstrated by comparison with samples of both products. Besides ethylidene diesters, highly coloured polyvinyl acetate was also isolated; its formation probably results from the initiation with BF_3.

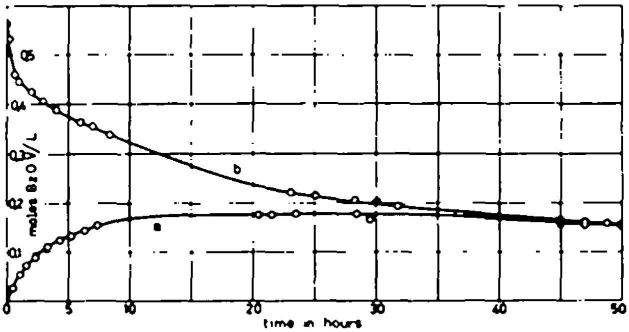
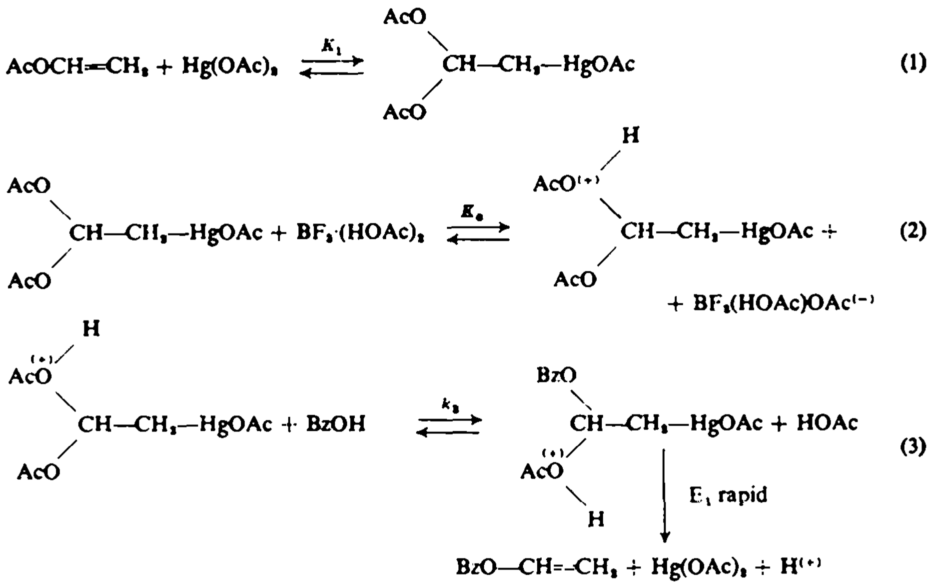


Fig. 7 Vinyl interchange reaction. 30° in EtOAc (8·982 M l^{-1})

(HgO) = 5·238 mM l^{-1} (BF_3) = 3·189 M l^{-1}
(BzOH) = 0·56 M l^{-1}
(AcOH) = 0·56 M l^{-1} BzOV × 0·56 M l^{-1}
(AcOH) = 0·178 M l^{-1} (AcOH) 0·7575 M l^{-1}
direct (a) inverse (b)

DISCUSSION

Based on the kinetic data and the results of the previous paper,[1] the following reaction mechanism can be proposed:



In the reaction scheme the first step consists in the selective addition of mercuric salt to vinyl acetate with formation of acetoxy mercury-ethylidene diacetate. Equilibrium (2) corresponds to the dissociation constant Ka of the conjugated acid of this mercury derivative. Reaction (3) is rate determining; it corresponds to the acid catalysed substitution of an acetic acid molecule by benzoic acid. The reaction product probably undergoes a rapid monomolecular elimination reaction.

Assuming that only a small fraction of the reactants are present in the form of the complex, the following rate expression can easily be derived,

$$R = k_3 K_1 Ka\ [\text{Vin OAc}]\ [\text{BzOH}]\ [\text{Hg(OAc)}_2]\ [\text{BF}_3\cdot(\text{HOAc})_2]$$

where K_1 and Ka correspond to the equilibrium constant of reactions (1) and (2) and k_3 the rate constant of step (3).

In reaction (3) the protonation of the acetoxy-ester group not only enhances the substitution process, but also the subsequent elimination reaction.

It is evident that this reaction scheme agrees completely with the data of NMR as described in the previous paper.

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