Kinetics of Methoxymercuration of trans-Cinnamic Acid and Methyl Cinnamate

William I. Awad, Boshra M. Awad, Nadia R. Guirguis and Afaf A. El-Beih

Department of Chemistry, University College for Women, Ain Shams University, Heliopolis, Cairo, Egypt.

The rates of methoxymercuration of trans-cinnamic acid and methyl cinnamate are determined by following up the change of concentration of the liberated acetic acid. The overall order of reaction is found to be a second order kinetics being first order with respect to each of the alkene and mercuric acetate. The reaction proceeds via three consecutive steps in which $[H^+]$ first increases with time, then decreases and finally increases again. The rate of the reaction is also determined by following up the change of the concentration of the inorganic mercury which represented only the formation of methoxymercuric acetate. The energies of activation are calculated.

It is well established that the reaction of mercuric salts in a protic solvent with an alkene affords an oxymercurial.[1-3] Many mechanisms have been suggested for methoxymercuration of alkenes which are (a) an ionic mechanism via an alkene mercurinium ion,[4] (b) a non-ionic mechanism,[5,6] or (c) a free radical mechanism.[3] Schrauth et al.[7] have shown that mercuric acetate adds to methyl cinnamate to give methyl β-methoxy-α-acetoxymercuric-hydrocinnamate.

Most of the kinetic studies for the methoxymercuration of different alkenes were carried out by following the change of the concentration of inorganic mercury.[3,8-12]

Adopting a different procedures in this investigation, it is planned to study the kinetics of methoxymercuration of alkenes with known geometrical configuration which are trans-cinnamic acid and methyl cinnamate by following up the change of $[H^+]$ due to liberation of acetic acid during the reaction.

EXPERIMENTAL AND RESULTS

Preparation of Methoxymercuric Acetate .- Dissolution of mercuric acetate (5 g) in absolute methanol,[13] then removal of the free acetic acid and excess methanol under vacuum gave methoxymercuric acetate,[5,9] (90% yield).

Procedures of Rate Measurements :

(a) Change of the Concentration of H^+ .- The rate of methoxymercuration of trans-cinnamic acid (0.001 M) with mercuric acetate (0.0125 M) was studied at 26° by following the change of the concentration of the liberated acetic acid, at different intervals of time by means of pH meter (PYE UNICAM), and also by titration of aliquots of 5 ml of the reaction mixture against standard (0.05 N) sodium carbonate solution using phenolphthalein as indicator. It was found that, on plotting either the pH values or the mls of carbonate at different intervals against time t, curves with three consecutive stages were obtained, in which $[H^+]$ increases, then decreases and finally

increases again. In each case a blank experiment with 0.001 M cinnamic acid was carried out. On repeating the measurements of the pH for solvolysis of mercuric acetate (0.0125 M) in methanol (i.e., without addition of alkene), the plot of pH values against time gave a straight line parallel to the first stage of the pH-time curve for the reaction (Fig. 1). The titration method was used throughout all the experiments.

Kinetic Measurements .- In every experiment, the required weight of the alkene was dissolved quantitatively in absolute methanol. The reaction flask was kept in a thermostat type [(EIN), -50° to $+30^{\circ} \pm 0.01^{\circ}$, Germany] adjusted at the required temperature. After attaining the thermal equilibrium, the appropriate weight of mercuric acetate was added and thoroughly mixed. Immediately, after mixing, a sample of 5 ml of the reaction mixture was withdrawn, placed in a conical flask containing 10 ml redistilled water, previously immersed in an ice-salt cooling mixture and then titrated against the standard titrant. This reading is considered as the zero reading. Samples of 5 ml of the reaction mixture were withdrawn at suitable intervals of time until at least 75% of the reaction was completed. The final reading was taken after sufficient time depending on the temperature and the alkene. Each run was repeated at least twice.

Order of the Reaction .- On using equimolars of both the alkene (0.001 M) and mercuric acetate (0.001 M) at 26°, the reaction was found to be of a second order kinetics overall,

first order with respect to each of the alkene and mercuric acetate; the molecular concentration of alcohol being considered constant. Thus, on using a relatively high molecular concentration of mercuric acetate (0.0125 M), the rate of the reaction became pseudo-first order with respect to the alkene. Hence, plotting log $\frac{a}{a-x}$ vs time (t) gave curves with three intercepting lines showing an increase of log $\frac{a}{a-x}$, followed by a decrease and then increases again. From these curves three velocity constants designated as k_1, k_2 and k_3 could be calculated, representing the three consecutive stages, respectively. This reaction was repeated at three different temperatures, 25°, 30° and 35°. Plotting log k for each stage against $\frac{1}{T}$ gave straight lines from which energies of activation could be calculated and from which the enthalpies and entropies of activation were conventionally calculated. The results obtained are given in Table 1.

Methoxymercuration with Prepared Methoxymercuric Acetate.- Studies of the rate of methoxymercuration of cinnamic acid (0.001 M) with prepared methoxymercuric acetate (0.001 M and 0.0125 M) at 23° in methanol show that with 0.001 M of mercuric salt, the reaction is of a second order kinetics; being first order with respect to each component. Plot of $(\frac{a}{a-x})$ against time (t) gave a curve with two intercepting straight lines. In the second case when 0.0125 M mercuric salt was used, plot of log $\frac{a}{a-x}$ vs (t) gave a curve with only two stages in which log $\frac{a}{a-x}$ decreases by time, then increases. Calculation of the velocity constants for this curve gave values of k_2 and

Table I. Velocity Constants and Activation Parameters for Methoxymercuration of trans-Cinnamic Acid and Methyl Cinnamate

	trans-Methyl Cinnamate			trans-Cinnamic Acid			
Temp. ^{o}C	k_1 min^{-1}	k_2 min^{-1}	k_3 min^{-1}	Temp. ^{o}C	k_1 min^{-1}	k_2 min^{-1}	k_3 min^{-1}
25	9.28×10^{-3}	5.70×10^{-2}	6.67×10^{-3}	20	5.62×10^{-3}	9.39×10^{-3}	4.31×10^{-3}
35	2.08×10^{-2}	8.48×10^{-2}	1.48×10^{-2}	26	9.71×10^{-3}	1.56×10^{-2}	6.14×10^{-3}
40	3.07×10^{-2}	1.03×10^{-1}	2.15×10^{-2}	36	2.33×10^{-2}	3.45×10^{-2}	1.07×10^{-2}
$E^{\#}$ k cal. $mole^{-1}$	14.9	7.3	14.5		16.1	14.5	10.1
$\Delta H^{\#}_{25^{o}}$ K cal $mole^{-1}$	14.4	6.7	13.9	$\Delta H^{\#}_{26^{o}}$	15.5	13.9	9.5
$-\Delta S^{\#}_{25^{o}}$ cal $degree^{-1}$	16.66	38.90	19.90	$-\Delta S^{\#}_{26^{o}}$	16.98	21.26	37.58

k_3 which are in accordance with the results obtained on using cinnamic acid and mercuric acetate in methanol under the same conditions. The results obtained are given in Table II. This fact indicates that the first step in the reaction with mercuric acetate represented the prior formation of methoxymercuric acetate.

Table II. Reaction of Cinnamic Acid (0.001 M) with Mercuric and Methoxymercuric Acetate (0.0125 M) at 23°.

Mercuric salt	k_2 min^{-1}	k_3 min^{-1}
Mercuric acetate	1.22×10^{-2}	5.16×10^{-3}
Methoxymercuric acetate	1.21×10^{-2}	5.05×10^{-3}

(b) Change of Inorganic Mercury Concentration.- The rate of methoxymercuration of cinnamic acid (0.001 M) was also followed up by measuring the change of concentration of the inorganic mercury by its titration at different time intervals against standard KCNS solution using ferric alum as an inidicator.[3] Different molecular concentration of mercuric acetate (0.001, 0.0125 and 0.035 M) were used. For equimolars, the reaction was found to be of a second order kinetics overall; being first order with respect to each component. Hence, using relatively high molecular concentration of mercuric acetate, the reaction became pseudo-first order with respect to the alkene. Plotting log $\frac{a}{a-x}$ against time (t) gave straight lines with only one stage from which the velocity constant k was calculated

On using 0.0125 M mercuric acetate, it was found that, under the same conditions, the value of k obtained was nearly equal to the value of k_1 representing the first stage when sodium carbonate was used as titrant, within a small range of experimental error. These results indicated that thiocyanate solution represents only the first step of this reaction in which the inorganic mercury is consumed to form methoxymercuric acetate. The results are given in Table III.

Table III. Comparison Between Titrations Using Sodium Carbonate and Potassium Thiocyanate as Titrants.

Titrant	Sodium Carbonate	Potassium Thiocyanate
Temp. °C	k_1 min^{-1}	k_1 min^{-1}
23	7.38×10^{-3}	7.55×10^{-3}
26	9.71×10^{-3}	1.00×10^{-2}
36	2.33×10^{-2}	2.49×10^{-2}
$E^{\#}$ Kcal $mole^{-1}$	16.09	16.70

(c) Other Procedures .- When the rate of this reaction was followed up by its titration against HCl in butanol using thymol blue as an indicator, it was found that, whatever the millilitres taken from the reaction mixture and at any interval, the colour of the indicator changes from red to yellow[14] after the addition of the same amount of HCl in butanol. The same result was also obtained on using a solution of indicator in methanol. It seems that the change in colour is produced as a result of the change of the pH of the solution from 2.8 to

1.2 by the addition of HCl. The same result was obtained by following the dithiazone method.[10,12]

DISCUSSION

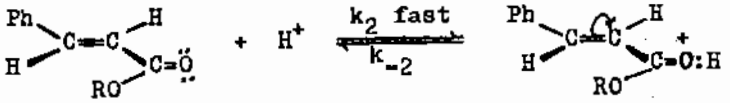
The data obtained reveal that the kinetic studies of methoxymercuration of alkenes by following the liberated acetic acid give s more detailed ides about the different steps involved in this reaction and the role of the proton. In all cases, a pH-time curve with three stages obtained indicating that methoxymercuration of cinnamic acid and methyl cinnamate takes place via three consecutive steps. The first step in which $[H^+]$ increases is attributed to the formation of methoxymercuric acetate which is formed by prior solvolysis of mercuric acetate by the alcohol.[5] This step is also represented by potassium thiocyanate and by change of the pH of the solvation of mercuric acetate in methanol with and without the alkene. This step is reversible whereby its rate is decreased by increasing the acidity of the medium. Wright and his coworkers[5] found that addition of acetic acid during methoxymercuration retarded the reaction, whereas removal of the free acetic acid from solution by some means accelerated it. They attributed it to further solvolysis. The first step can be represented as :

$$MeOH + Hg(OAc)_2 \underset{k_{-1}}{\overset{k_1 \text{ fast}}{\rightleftharpoons}} Me\text{—}\ddot{O}\text{—}Hg\text{-}OAc + H^+ + {}^-OAc$$

In the second step, the $[H^+]$ decreases, i.e., an uptake of protons occurs that becomes detectable around a critical

pH (viz. pH .5.7). This step is also reversible and the velocity constant of this step is represented as k_2. The rate of this step increases by decreasing the $[H^+]$ of the medium. This means that protonation enhances the reaction and must play an important role. If the proton is taken by the formed methoxymercuric acetate, the rate will be independent on the alkene used which is not the case. Here we have to differentiate between the methoxymercuration of ordinary olefins and that of α,β-unsaturated carbonyl compounds. In the case of ordinary olefins, e.g. stilbene,[8] 1- and 2-pentenes[15] the reaction is generally very slow and not accelerated by acids,[8] and cis-form reacts faster than the trans-one. However, α,β-unsaturated carbonyl compounds[16] react much more rapid with a regiospecific entrance of the Hg- atom at the α-carbon atom.

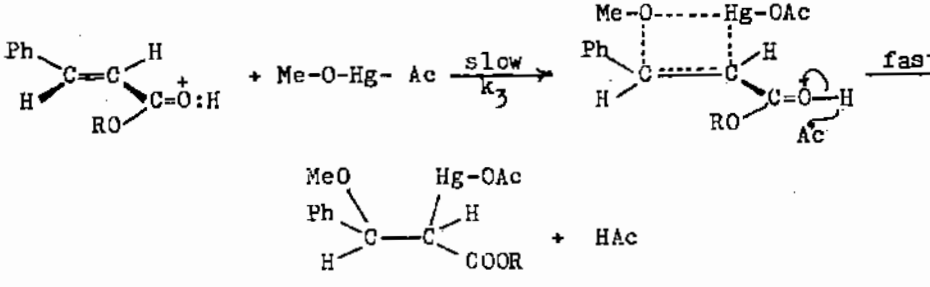
The compounds investigated here are of the latter type and protonation (uptake of proton) can take place on the lone pair of electrons of the oxygen which is conjugated with the double bond. This clearly increases the polarity of the double bond and highly facilitates methoxymercuration. This step is substantiated by the fact that no reaction occurs with the prepared methoxymercuric acetate in aprotic solvent (dioxane) except after protonation with formic acid. This step can be represented as follows :



R = H or CH_3 Protonated complex

The idea of the association of polarity with the increase in rate of reaction can also interpret why cis-isomers (more polar) react faster than trans-ones[8,15] (less polar).

The third step which is slow and the rate determining step is irreversible one. Its rate is represented as k_3. Since the reaction is a second order overall, first order with respect to both of the alkene and methoxymercuric acetate, it is convenient to propose a transition state containing these two species. In this step $[H^+]$ increases indicating that the addition of methoxymercuric acetate to the activated protonated complex takes place with the liberation of the proton. This is supported by the fact that this step is accelerated by decreasing the $[H^+]$ of the medium and this may explain why the energy of activation in case of cinnamic acid is lower than that for methyl cinnamate in this stage. This step is a concerted process ($2\pi + 2\sigma$ cycloaddition reaction) going through a four-membered transition state. The low entropies of activation favours this mechanism. This is in accordance with that mechanism suggested by Wright et al.[3,7,10] for methoxymercuration of cyclohexene. The third step can be represented as follows:



REFERENCES

1. L.T. Sandborn and C.S. Marvel, J. Amer. Chem. Soc., 48 1409 (1926).

2. W. Schrauth, W. Schoeller and R. Struenser, Ber., 43, 695 (1910).

3. G.F. Wright, J. Amer. Chem. Soc., 57, 1993 (1935).

4. M.L. Lucas, F.R. Heper and S. Winstein, J. Amer. Chem. Soc., 61, 3102 (1939).

5. A. Rodgman and G.F. Wright, J. Org. Chem., 17, 988 (1953), J. Amer. Chem. Soc., 69, 797 (1947).

6. W. Manchat, Ber., 53, 984 (1920).

7. W. Schrauth, W. Schoeller and R. Struenser, Ber., 44, 1048 (1911).

8. A.M. Birks and G.F. Wright, J. Amer. Chem. Soc., 62, 2412 (1940).

9. W.H. Brown and G.F. Wright, J. Amer. Chem. Soc., 62, 1991 (1940).

10. J. Romeyn and G.F. Wright, J. Amer. Chem. Soc., 69, 687 (1947).

11. G.F. Wright, Cand. J. Chem. Soc., 33, 1002 (1955).

12. M.L. Mallik and M. Nadas, J. Amer. Chem. Soc., 82, 4269 (1960).

13. A.I, Vogel, "Practical Organic Chemistry", Longmans Green Co., p. 167 (1948).

14. I.M. Kathoff and E.B. Sandell, "Text Book of Quantitative Inorganic Analysis", New York, MacMillan Co., p. 541 (1967).

15. H.C. Brown and P.J. Geoghegan Jr., J. Org. Chem., 37, 1937 (1972).

16. A.J. Blood Worth and R.J. Bunce, J. Chem. Soc. (D) 753 (1970).

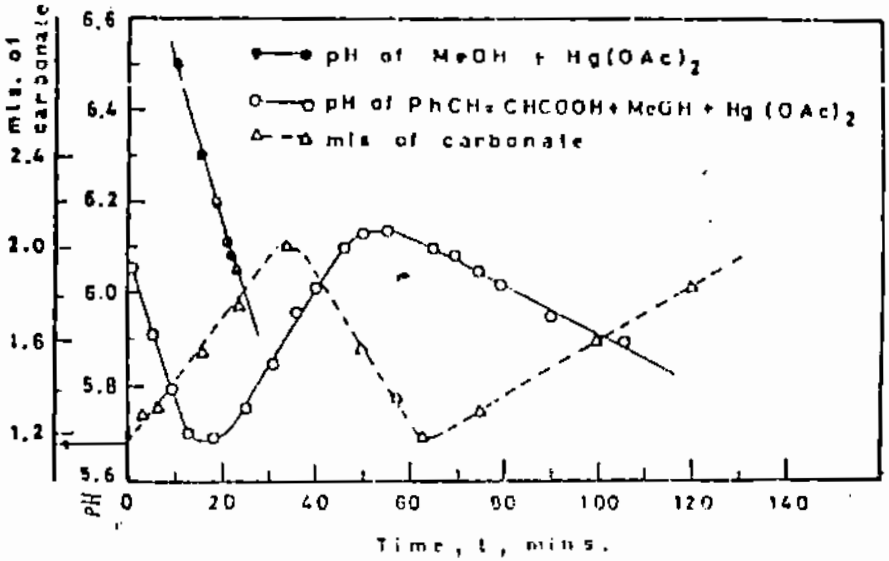


Fig. 1

Change of $[H^+]$ with time

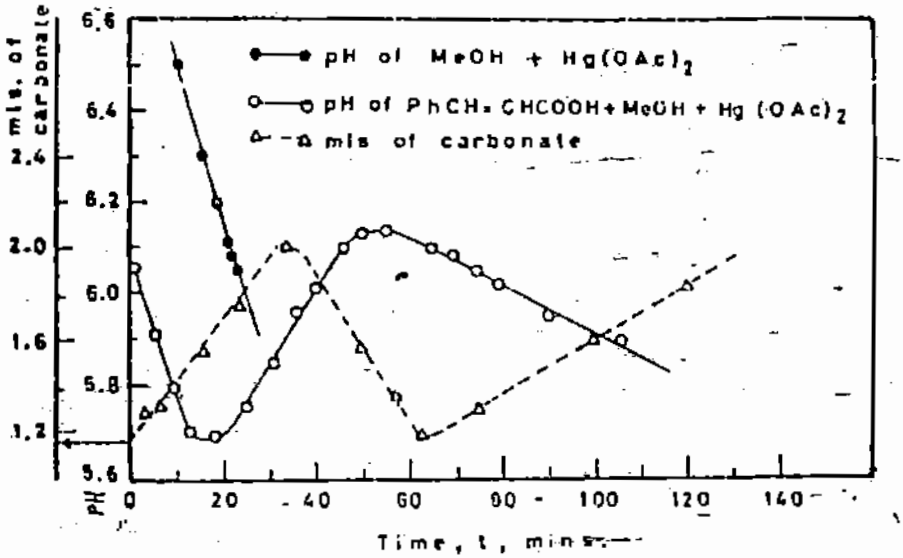


Fig. 1

Change of $[H^+]$ with time