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METHOXY-MERCURATION OF METHACRYLIC AND CINNAMIC ESTERS AND CINNAMALDEHYDE

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Abstract—The methoxymercuration of methyl and ethyl methacrylates, ethyl cinnamate and cinnamaldehyde has been kinetically studied in the temperature range 35°–50°. Second-order kinetics has been observed for the over-all reaction. In all the cases, the reaction is appreciably accelerated by acetic acid and strongly retarded by sodium acetate and nitrogen bases. The results indicate an ionic mechanism involving a reactive carbonium ion as an intermediate formed by interaction between the unsaturated compound and undissociated mercuric acetate.

Two different mechanisms, one ionic and the other non-ionic, are reported to operate in the oxy-mercuration of different types of unsaturated compounds.[1] Wright proposed a non-ionic mechanism for the methoxy-mercuration of methyl cinnamate,[1a] and later Wright *et al.* carried out extensive studies in this field, and have established the non-ionic mechanism for the oxy-mercuration of cyclohexene and 2,6-dimethyl hepten-5-ol-2.[1b–1d] Recently, however, they have found that with norbornene,[1e] the reaction proceeds through an ionic mechanism, presumably by way of an "alkene-mercurinium" ion, as suggested, much earlier by Lucas *et al.*[1f]. Mallik and Das,[1g] who studied the methoxy-mercuration of acrylic esters, obtained definite evidence in favor of the ionic mechanism. Further studies have been undertaken in this field, and the present paper reports the results on the methoxy-mercuration of methacrylic and cinnamic esters and cinnamaldehyde.

EXPERIMENTAL

Materials. The samples of methyl and ethyl methacrylates were purified by the usual procedure.[2] A sample of analytical grade (B.D.H.) *trans*-ethyl cinnamate was distilled under red. press. in an all-glass apparatus, the middle fraction being used for the kinetic studies. A sample of analytical *trans*-cinnamaldehyde grade (Naarden) was purified by distillation under red. press., the distilled samples being stored in a refrigerator in a colored bottle to avoid oxidation. The purification of other materials and preparation and standardization of solutions used for the work were similar to those reported earlier.[1g]

Kinetic measurements. Reaction rates were measured mostly at 45°, with some runs being carried out at 35°, 40° and 50°. The maximum variations in the temp of the thermostat during a run were ±0·05°.

The initial concentrations of the olefinic substances in the reaction mixtures depended on the reaction rates. The rate with the methacrylic esters being rather slow, higher concentrations (0·1–0·6 M) had to be used to obtain measurable speeds. For ethyl cinnamate and cinnamaldehyde, the initial

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[1a] G. F. Wright, *J. Amer. Chem. Soc.* **57**, 1993 (1935); [b] J. Romeyn and G. F. Wright, *Ibid.* **69**, 697 (1947); [c] A. G. Brook, A. Rodgman and G. F. Wright, *J. Org. Chem.* **17**, 988 (1952); [d] A. Rodgman and G. F. Wright, *Ibid.* **18**, 1617 (1953); [e] M. J. Abercrombie. A. Rodgman, K. R. Bharucha and G. F. Wright, *Canad. J. Chem.* **37**, 1328 (1959); [f] M. J. Lucas, F. R. Hepner and S. Winstein, *J. Amer Chem. Soc.* **61**, 3102 (1939); [g] K. L. Mallik and M. N. Das, *Ibid.* **82**, 4269 (1960).

[2] Riddle, *Monomeric Acrylic Esters.* Reinhold (1954).

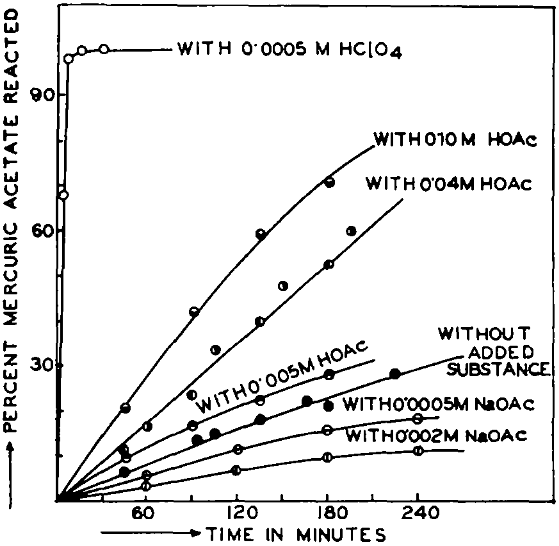

FIG. 1. Reaction between cinnamaldehyde (0·05 M) and mercuric acetate (0·025 M) at 45°.

concentrations were in the range 0·05–0·10 M. As mercuric acetate has limited solubility in methanol, the highest concentration that could be conveniently used was 0·05 M, the lowest (0·01 M) being determined by the accuracy of the analytical method employed for the reaction, described earlier.[1g]

RESULTS

The kinetic results obtained for all the olefinic compounds studied indicate good agreement with second-order kinetics according to the relationships

$$kt = \frac{2{\cdot}303}{a-b}\log\frac{b(a-x)}{a(b-x)},$$

where a and b are the initial concentrations of the reactants, and

$$kt = \frac{1}{a-x} - \frac{1}{a},$$

for equimolar concentrations of the reactants.

The rate constants (k) for the methoxy-mercuration of the four olefines are shown in Tables 1–4. The rates for methyl methacrylate were measured at three temperatures (Table 1) and the activation energy as calculated from the results to the nearest kilocalorie are 15 kcals/mole, as compared with 9 kcals/mole for methyl acrylate.[1g] The rate constant for the methoxy-mercuration of methyl methacrylate may be approximately represented by the equation $k = 2{\cdot}3 \times 10^8 \times e^{-15000/RT}$. Ethyl methacrylate was studied only at 45°, and the rate constant (0·016 litre-mole^{-1} min^{-1}) is found to be of the same order of magnitude as that for methyl methacrylate (0·013) at the same temperature, this being about one-tenth of the rate constant for the acrylic esters (1 g).

The rate constants for ethyl cinnamate and cinnamaldehyde are, in their turn, very nearly identical (0·03 litre-mole^{-1} min^{-1}) at 45°, being roughly twice the values

TABLE 1. RATE CONSTANTS FOR REACTION BETWEEN METHYL METHACRYLATE AND MERCURIC ACETATE

Concentration of reactants (mole per l.)			
Mercuric acetate	Methyl methacrylate	Added substances with concentration (mole per l.)	$k \times 10^2$ l mole-min.$^{-1}$
		Temperature 40°	
0·025	0·50	None	0·96
0·025	0·50	None	0·93
		Temperature 50°	
0·025	0·50	None	1·97
0·021	0·50	None	2·01
		Temperature 45°	
0·025	0·467	None	1·37
0·025	0·50	None	1·34
0·016	0·623	None	1·34
0·016	0·623	None	1·35
0·025	0·46	Acetic acid (0·12)	1·51
0·025	0·468	Sodium acetate (0·0002)	0·375
0·0159	0·59	Sodium acetate (0·002)	0·137
0·0167	0·623	Sodium propionate (0·001)	0·276
0·0159	0·59	Triethanolamine (0·002)	0·252
0·025	0·468	Pyridine (0·0016)	0·240

TABLE 2. RATE CONSTANTS FOR REACTION BETWEEN ETHYL METHACRYLATE AND MERCURIC ACETATE AT 45°

Concentration of reactants (mole per l.)			
Mercuric acetate	Ethyl methacrylate	Added substances with concentration (mole per l.)	$k \times 10^2$ l mole^{-1}min^{-1}
0·050	0·414	None	1·60
0·030	0·193	None	1·61
0·030	0·200	Acetic acid (0·30)	0·46
0·030	0·180	Sodium acetate (0·112)	2·45

obtained for the methacrylic esters. Ethyl cinnamate was studied at two temperatures, 35° and 45°, and the activation energy, as calculated from the temperature coefficient, is approximately 8·5 kcals/mole.

Reaction in the presence of added substance

The rates of the methoxy-mercuration of all the four olefines were measured at 45° in the presence of perchloric acid, acetic acid and anionic as well as nitrogen bases. The observations are essentially similar to those recorded for acrylic esters.[1g]

Effect of perchloric acid. The addition of mercuric acetate to all these substances is very strongly catalysed by perchloric acid, the rates being too fast for kinetic measurements even with as low as 0·0005 N acid. In the presence of 0·004–0·005 N perchloric acid, with 0·025 M reactants, quantitative reaction occurs in

TABLE 3. RATE CONSTANTS FOR REACTION BETWEEN ETHYL CINNAMATE AND MERCURIC ACETATE

Concentration of reactants (mole per 1.) Mercuric acetate	Ethyl cinnamate	Added substances with concentrations (mole per 1.)	$k \times 10^3$ 1 mole^{-1}min^{-1}	
		Temperature 35°		
0·025	0·050	None	1·96	
0·025	0·050	None	1·96	
		Temperature 45°		
0·025	0·050	None	3·09	Mean 3·04 ± 0·03
0·025	0·050	None	3·02	
0·025	0·050	None	3·05	
0·025	0·050	None	3·05	
0·025	0·050	None	2·98	
0·025	0·025	None	3·02	
0·025	0·05	Acetic acid (0·04)	3·38	
0·025	0·025	Acetic acid (0·10)	3·41	
0·025	0·050	Sodium acetate (0·0005)	0·96	
0·025	0·050	Sodium acetate (0·002)	0·39	
0·025	0·050	Triethanolamine (0·005)	0·98	

TABLE 4. RATE CONSTANTS FOR REACTION BETWEEN CINNAMIC ALDEHYDE AND MERCURIC ACETATE AT 45°

Concentrations of reactants (mole per 1.) Mercuric acetate	Cinnamic aldehyde	Added substances with concentrations (mole per 1)	$k \times 10^3$ 1 mole^{-1}min^{-1}	
0·025	0·050	None	2·86	
0·025	0·050	None	3·05	Mean 3·00 ± 0·07
0·025	0·050	None	3·00	
0·025	0·050	None	3·10	
0·025	0·025	None	2·95	
0·025	0·025	None	3·06	
0·025	0·050	Acetic acid (0·005)	4·05	
0·025	0·050	Acetic acid (0·02)	7·25	
0·025	0·050	Sodium acetate (0·0005)	2·03	
0·025	0·050	Sodium acetate (0·002)	1·11	
0·025	0·050	Triethanolamine (0·0005)	2·10	

less than 30 min, for all these olefines at room temperature. The catalysed addition has, in fact, been utilized earlier for quantitative estimation of several methacrylic esters.[3] For cinnamaldehyde, the progress of reaction with time in the presence of perchloric acid and other added substances is graphically shown in Fig. 1, as an illustration.

Effect of added acetic acid. The reaction in all the cases is catalysed by added acetic acid, the effect being much more pronounced with cinnamaldehyde than with

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[3] K. L. Mallik and M. N. Das, *Chem. & Ind.* 162 (1959).

the esters. Thus, with 0·025 M mercuric acetate and 0·05 M cinnamaldehyde in the presence 0·005 M acetic acid, the rate constant at 45° is 0·0405 litre-mole^{-1} min^{-1}, as compared with the value of 0·030 in the absence of any added substance. With 0·02 M acetic acid, the rate constant increases to 0·0725 which is more than two and a half times the normal value. The reaction is still in fairly good agreement with second-order kinetics, but with higher concentrations (0·04–0·1 M) of acetic acid, marked deviations from second-order kinetics are observed. With 0·04 M and 0·1 M acetic acid, about 55% and 70% respectively of the mercuric acetate is added in three hours, as compared with less than 25% in the absence of acetic acid under otherwise identical conditions (Fig. 1).

For ethyl cinnamate, the accelerating effect of acetic acid is relatively smaller. With 0·025 M reactants, 0·04 M acetic acid raises the rate constant to 0·0338 litre-mole^{-1} min^{-1} from the normal value of 0·0304. On increasing the acetic acid concentration to 0·1 M, the rate constant (0·0341) remains virtually the same.

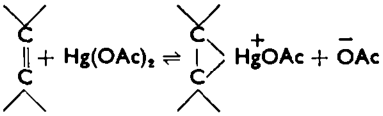
For the methacrylic esters, the catalytic effect of acetic acid is smaller still, but unmistakable. Thus, with 0·025 M mercuric acetate and 0·46 M methyl methacrylate in the presence of 0·01 M acetic acid, no appreciable change in the reaction rate was observed, but on increasing the acid concentration to 0·12 M, the rate constant showed a small, but definite, increase to 0·0151 litre-mole^{-1} min^{-1} from the normal value of 0·0136. For the reaction with 0·020 M ethyl methacrylate and 0·030 M mercuric acetate, the rate constant, in the presence of 0·30 M acetic acid, increases from 0·0160 to 0·0246 litre-mole^{-1} min^{-1}.

Effect of acetate and other bases. As with acrylic esters, anionic as well as nitrogen bases exert a pronounced retarding effect on the methoxy-mercuration of all the compounds studied (Tables 1–4). Not only acetate but propionate also retards the rate, and nitrogen bases like triethanolamine and pyridine exert an almost equally strong retarding effect.

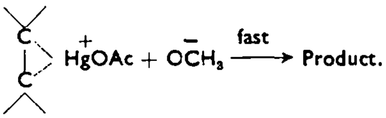
With as low as 0·00018 M sodium acetate the rate constant, obtained with 0·025 M mercuric acetate and 0·468 M methyl methacrylate, drops down to $3{\cdot}75 \times 10^{-3}$ litre-mole^{-1} min^{-1} from the normal value of $13{\cdot}5 \times 10^{-3}$. With the reactants at 0·016 M and 0·59 M respectively, the rate constant, in the presence of 0·002 M sodium acetate, is nearly one-tenth of the normal value. For ethyl cinnamate also, 0·002 M sodium acetate decreases the rate constant to nearly one-eighth the normal value, using the olefine and mercuric acetate at 0·05 M and 0·025 M respectively. For cinnamaldehyde, the effect is relatively smaller, though quite pronounced (Fig. 1, Table 4). This fact may be considered significant, when combined with the higher catalysing effect of acetic acid observed with this olefine as reported above. Apparently, acetic acid simultaneously exerts two opposing effects on the reaction rate. The acetate ions generated from the added acid may be expected to exercise a retarding influence, thus opposing to some extent the operation of acid-catalysis. For cinnamaldehyde, the retarding effect of the acetate ion being relatively smaller, the overall catalysing effect of acetic acid appears stronger.

DISCUSSION

The general features of the methoxy-mercuration of the olefines studied are essentially similar to those observed for acrylic esters.[1a] The catalysing effect of acetic acid combined with the rather pronounced retarding effect of the acetate ion (and other bases) is indeed very significant and provides a piece of crucial evidence in favor of an ionic mechanism. If the reaction occurred through a non-ionic mechanism involving the addition of methoxy-mercuric acetate (formed by solvolytic reaction with methanol) to the olefine, acetic acid would certainly retard, rather than accelerate, the reaction by suppressing the solvolysis. In fact, Wright *et al.* have actually observed that for cyclohexene and dimethylheptenol, added acetic acid retards the oxy-mercuration, while the removal of acetic acid, formed during the reaction, by evaporation increases the rate. The pronounced retarding effect exerted by bases as observed in the present study, should also be quite unexpected if the reaction occurred through a non-ionic mechanism. The consistent results obtained with acrylic, methacrylic and cinnamic esters and cinnamaldehyde unmistakably lead to the conclusion that the reaction in all these cases proceeds through an ionic mechanism, possibly by way of an "alkene-mercurinium" ion,[1f] formed by interaction between molecular (undissociated) mercuric acetate and the olefine. The detailed reasonings leading to this conclusion were set forth earlier[1g] and need not be reproduced here. The mechanism may be represented as follows:



The cation then rapidly reacts with the solvent or more probably with a methoxy ion (generated by self ionization of methanol) to give the final product.



As early as 1935, Wright[1a] suggested a non-ionic mechanism for the methoxy-mercuration of methyl cinnamate chiefly on the ground that the *cis* and *trans* forms give the respective racemic products in the pure state. But it is now well-known that an ionic mechanism is not necessarily inconsistent with the stereospecificity of a reaction. The reactive cation, as represented above, is probably a π-complex and may well contain a three-membered ring which is rigid enough to make possible the maintenance of the configuration.

Wright *et al.*,[1e] who have shown the oxy-mercuration of norbornene as occurring through an ionic mechanism, consider this reaction as "abnormal". They have concluded that the ionic mechanism can occur only for those alkenes in which an electron field distortion is possible, as in a bicyclic alkene like norbornene. The present studies indicate that possibly the oxy-mercuration of α,β-unsaturated carbonyl compounds in general also proceeds through an ionic mechanism. The reason may lie in the electronic distribution peculiar to such conjugated systems.

The C=O group conjugated to an ethylenic system deactivates the C=C bond towards electrophilic reagents, and hence it is quite expected that these compounds should undergo methoxy-mercuration (which undoubtedly involves electrophilic addition irrespective of the actual mechanism) at rates much slower than olefines which do not contain such deactivating groups. The relative rates for these olefines which have been studied are found to lie in the order: acrylic esters > cinnamic ester ≈ cinnamic aldehyde > methacrylic esters. It might be expected that in the methacrylic and cinnamic esters, the α-methyl and β-phenyl groups would cause electron accession towards the C=C bond making it more susceptible towards methoxy-mercuration. The slower rates actually observed for these substances may be ascribed to steric factors. But curiously enough, the activation energy for methyl methacrylate (15 kcals/mole) is found to be much higher than that for methyl acrylate (9 kcals/mole), and the frequency factor also is at the same time unexpectedly higher for the methacrylate ($2{\cdot}3 \times 10^8$ litre-mole^{-1} min^{-1}) than for the acrylate ($2{\cdot}0 \times 10^5$). The higher activation energy may perhaps be attributed to the possibility of the methyl group hyperconjugating with the C=C group, which tends to make it more stable. The frequency factors indicate that the entropy of activation ($\Delta S^{\ddagger}$) for the reaction with the acrylate is more negative than that for the methacrylate by nearly 7 cals deg^{-1} mole^{-1}. For the cinnamic ester, however, the activation energy (8·5 kcals/mole) as well as the frequency factor ($1{\cdot}95 \times 10^4$), as roughly obtained from rate measurements only at two temperatures, is quite in line with our expectations.