Table VIII illustrates the kinetic behavior observed on solvolysis of α-phenyl-γ-methylallyl *p*-nitrobenzoate. A fast initial rate was observed (63 min. half-life) followed by a much slower reaction (131 hr. half-life). The rate constants for the initial fast reaction have been calculated from the experimental infinity titer. The rate constants for the slower reaction were calculated from the theoretical infinity titer.

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Methoxy-mercuration of Acrylic Esters

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RECEIVED JUNE 8, 1959

Methoxy-mercuration of methyl acrylate has been studied kinetically over the temperature range 35–50°. Second-order kinetics has been observed for the over-all reaction, the energy of activation being about 9 kcal./mole. The reaction is slightly accelerated by acetic acid, and strongly retarded by sodium acetate, propionate and butyrate. Nitrogen bases also exert an equally strong retarding effect on the reaction. The reaction with ethyl and butyl acrylates was studied at 45° and found to exhibit exactly similar features. The results strongly favor an ionic mechanism for the addition, involving the formation of a reactive carbonium ion by interaction between the unsaturated compound and undissociated mercuric acetate.

Mercuric salts have long been known to form addition products with unsaturated compounds, the reaction being generally very fast in methanol. Extensive and systematic studies have been conducted on some oxy-mercuration reactions by Wright and co-workers,[1] especially on methoxy-mercuration of cyclohexene. The rapid and quantitative addition of mercuric acetate to several unsaturated compounds in methanol has been utilized to a limited extent for the estimation of these compounds.[2] Vinyl and allyl esters readily react with mercuric acetate in methanol, but with acrylic and methacrylic esters the addition is much slower in the absence of catalysts. It seemed of interest to study this reaction with different types of substituted ethylenes in order to determine the effect of substituent groups which is expected to be of great help in elucidating the mechanism of the reaction. The present paper reports the results of kinetic studies on the addition of mercuric acetate to methyl, ethyl and butyl acrylates in methanol.

Experimental

Materials.—The acrylic esters were purified by the following procedure. The samples were repeatedly washed with caustic soda till free from inhibitors, and then were washed with distilled water. After drying with calcium chloride, the samples were fractionally distilled under reduced pressure in all-glass apparatus, the middle fraction being collected for the work. Only freshly distilled samples were used for the kinetic studies, the absence of peroxides being tested for with potassium iodide.

Mercuric acetate was prepared by dissolving pure mercuric oxide in reagent grade glacial acetic acid. The solution was carefully evaporated almost to dryness, and allowed to cool. The residue was kept in a vacuum desiccator for several days to remove the last traces of water and acetic acid. The sample of mercuric acetate so obtained was analyzed for purity by direct titration in propylene glycol–chloroform with standard hydrochloric acid in butanol, using thymol blue as indicator.[3] The purity was also checked by direct titration with standard alkali in aqueous acetone with phenolphthalein as indicator and further checked by titrating with standard nitric acid the alkali liberated by addition of potassium iodide.[4] The agreement between the alkali and acid titers indicated absence of free acid and also of basic acetate. The titration results indicated a purity of about 99.8%.

Extra pure methanol (Merck) was used as the reaction medium without any further treatment; $0.01-0.02N$ hydrochloric acid in butanol was used for the titration, being standardized against mercuric oxide after conversion to acetate.[2c]

Sodium acetate, propionate and butyrate solutions were prepared by dissolving reagent grade sodium carbonate in the respective acids, the excess acid being removed by evaporation. The sodium salts so obtained were dissolved in methanol and the solutions were analyzed by non-aqueous titration with standard hydrochloric acid in butanol, using thymol blue as indicator.

Triethanolamine and pyridine solutions were prepared by dissolving analytical grade reagent in methanol and standardized by titration with hydrochloric acid in butanol.

Solutions of acrylic esters and of mercuric acetate were prepared by weighing out the reactant into a measured volume of methanol, so as to give the desired concentrations.

Kinetic Measurements.—Reaction rates were measured at 35, 40, 45 and 50°. A larger range of temperature was precluded by experimental difficulties. The thermostat used for the work maintained a temperature with a maximum variation of ±0.05°. Most of the work was confined to 45°, and at this temperature, the initial concentration of mercuric acetate was in the range of 0.01–0.04 g. mole/liter, and for methyl acrylate the concentration was in the range of 0.01–0.22 g. mole/liter. The solutions of the reactants of desired concentrations were separately prepared in Jena bottles with glass stoppers and kept in the thermostat to attain the bath temperature. Equal volumes (usually 20 ml.) of each were then mixed together in a Jena bottle and the reaction was followed by analyzing 5-ml. portions of the mixture by titration with hydrochloric acid in butanol, using thymol blue as indicator.

Analytical.—The analytical method used is essentially based on the fact that one mole of mercuric acetate when titrated with hydrochloric acid in glycolic or alcoholic media consumes two equivalents of acid, whereas the mercurated product formed by addition takes up only one equivalent of acid per mole.[2c,2d] If v_0 ml. is the initial acid titer, and v ml. the titer at time t for 1 ml. of the reaction mixture and if N be the normality of the hydrochloric acid, the concentration of mercuric acetate at any stage is given by $(v - {}^1/_2\, v_0)N$ g. moles/liter.

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[1] (a) T. Connor and G. F. Wright, THIS JOURNAL, **68**, 256 (1946); (b) A. G. Brook, A. Rodgman and G. F. Wright, *J. Org. Chem.*, **17**, 988 (1952); (c) A. Brook and G. F. Wright, *Can. J. Res.*, **28B**, 623 (1950); **29**, 308 (1951); (d) G. F. Wright, *Chem. in Canada*, **2**, 149 (1950); (e) W. R. R. Park and G. F. Wright, *Can. J. Chem.*, **12**, 1088 (1957); (f) A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 1617 (1953); (g) A. Rodgman, D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **36**, 1377 (1957).

[2] (a) R. P. Marquardt and E. W. Luce, *Anal. Chem.*, **20**, 751 (1948); **21**, 1195 (1949); (b) R. N. Martin, *ibid.*, **21**, 921 (1949); (c) M. N. Das, *ibid.*, **26**, 1086 (1954); (d) K. L. Mallik and M. N. Das, *Chemistry & Industry*, 162 (1959).

[3] M. N. Das, *J. Indian Chem. Soc.*, **31**, 39 (1954).

[4] M. N. Das, *Anal. Chem.*, **25**, 1406 (1953).

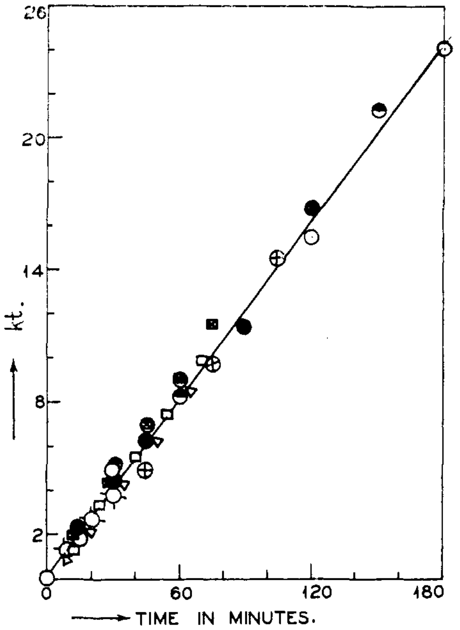


Fig. 1.—Reaction between mercuric acetate and methyl acrylate at 45°.

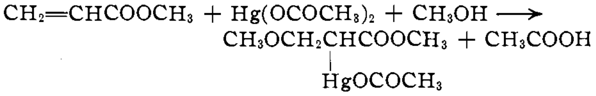
	Mercuric acetate, *M*	Methyl acrylate, *M*		Mercuric acetate, *M*	Methyl acrylate, *M*
□	0.025	0.05	⧖	0.025	0.216
△	.025	.06	○	.025	.025
⊕	.0125	.03	●	.025	.025
☒	.0125	.04	◓	.025	.0125

For the runs carried out in the presence of an added base or mineral acid, appropriate corrections were applied to the observed acid titer. For the runs carried out in the presence of mineral acids, the titration with hydrochloric acid was done after adding a few drops of a saturated solution of sodium chloride in ethylene glycol to the sample.[2d]

Direct titration of the reaction mixture with thiocyanate was found to give erratic analytical results. Attempts were made to analyze the reaction mixture by diluting with water and extracting the organic mercury with chloroform, but quantitative extraction could not be effected by this procedure, and hence the method failed.

Results

Methoxy-mercuration of Methyl Acrylate.—Methyl acrylate is known to react with mercuric acetate in methanol to give the methyl ester of α-acetoxy-mercuri-β-methoxypropionic acid. This reaction has been utilized by Carter and West[5] for the preparation of α-amino-β-hydroxypropionic acid, using methyl acrylate as the starting material. By taking equimolecular amounts of mercuric acetate and methyl acrylate in methanol, and treating the reaction product with potassium bromide and bromine, they obtained 81–86% yield of pure β-methoxy-α-bromopropionic ester together with 5–10% of the dibromo derivative. This indicates that the β-methoxy-α-mercuriacetoxy derivative is the major, if not the only, product of the primary addition of mercuric acetate to methyl acrylate in methanol as



$$CH_2{=}CHCOOCH_3 + Hg(OCOCH_3)_2 + CH_3OH \longrightarrow CH_3OCH_2\underset{\displaystyle HgOCOCH_3}{\underset{|}{C}}HCOOCH_3 + CH_3COOH$$

The addition of mercuric salts to ethylenes are generally believed to be reversible leading to a state of equilibrium, although attempts at reaching this state from the reverse direction are generally reported to have been unsuccessful.[1,6] Rodgman, Shearer and Wright[1g] have, however, recently demonstrated the reversibility and studied the kinetics of de-oxymercuration.

Methoxymercuration of methyl acrylate using 0.025 *M* concentrations appears to stop after about 90% reaction, as determined by titration, and at water-bath temperature over several hours the reaction could not be forced beyond 93% completion. Attempts to isolate the organomercurial by distillation failed owing to decomposition, but the crude material obtained by chloroform extraction, after removal of the chloroform under vacuum, appeared by titration with hydrochloric acid in butanol to be 97% pure. This material in methanol (0.03 *M*) and an equivalent of acetic acid gave a constant titer over several days. While the fact that the reaction does not proceed to more than 90–93% completion, it seems to indicate that an equilibrium may be reached. The latter data suggest that no equilibrium is involved. Thus the question is not resolved. Side reactions may account, at least in part, for the apparently non-quantitative nature of the reaction, but these are perhaps relatively unimportant during the early stages of the reaction and should not, therefore, introduce any complications in the kinetic studies, if restricted to the stages of low conversion (20–30%).

Kinetics.—The kinetic results indicate agreement with second-order kinetics according to the usual relationships. Typical kinetic data for reaction at 45° are shown in Fig. 1.

The values of the specific rate constant (k) at various temperatures are presented in Table I. The rate constants have been computed from the slopes of the linear plots of the values of kt *versus* t. As the reaction progresses, deviations from simple second-order kinetics have often been observed, and hence for computing the rate constants, the reaction has generally been restricted to below 30%.

Table I

Rate Constants for Reaction between Methyl Acrylate and Mercuric Acetate

Concn. of the reactants (mole per l.)		Rate constant $k \times 10$, l. mole^{-1} min.$^{-1}$	Concn. of the reactants (mole per l.)		Rate constant $k \times 10$, l. mole^{-1} min.$^{-1}$
Mercuric acetate	Methyl acrylate		Mercuric acetate	Methyl acrylate	
Temperature 50°			.025	.216	1.35
0.025	0.025	1.83	.04	.10	1.34
0.025	0.025	1.83	Temperature 40°		
Temperature 45°			0.025	0.025	1.14
0.0125	0.0125	1.38	0.025	0.025	1.16
.0125	.03	1.38	Temperature 35°		
.0125	.04	1.38	0.0125	0.0125	0.88
.025	.025	1.32	.025	.025	.84
.025	.025	1.35	.025	.05	.86
.025	.050	1.35	.025	.025	.85
.025	.060	1.32	.025	.055	.86

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[5] H. E. Carter and H. D. West, *Org. Syntheses*, **20**, 81 (1940).

[6] J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

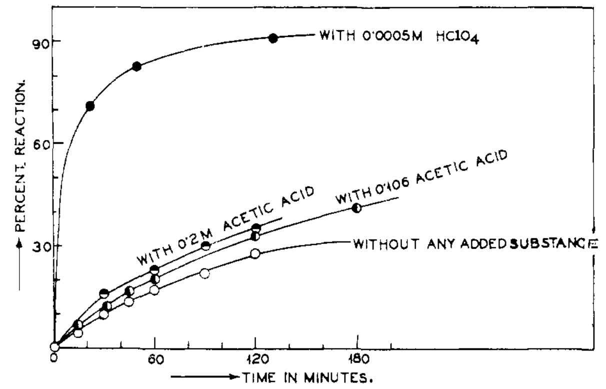

Fig. 2.—Reaction between 0.025 *M* methyl acrylate and 0.025 *M* mercuric acetate at 45°.

For the purpose of determining the activation energy the reaction was studied at four temperatures, 35, 40, 45 and 50°. The activation energy was calculated from the slope of the line obtained by plotting the logarithm of the average value of the rate constant, against the reciprocal of the absolute temperature. The value of the activation energy so calculated to the nearest kilocalorie is 9 kcal./mole.

Reaction in the Presence of Added Substances. Effect of Perchloric and Nitric Acids.—Perchloric and nitric acids exert a pronounced accelerating effect on the reaction rate. Using 0.001 *M* nitric acid with 0.025 *M* reactants at 45°, the reaction proceeds to 63% in 20 minutes, whereas in absence of the catalyst only about 6% addition occurs during the same period. Perchloric acid also exerts a very strong accelerating effect on the reaction rate, and with as low as 0.0005 *M* of this acid under otherwise identical reaction conditions as stated above, about 70% addition occurs in 20 minutes. Nearly quantitative addition at 45° has been found to occur in less than 30 minutes using 0.005 *M* perchloric acid with the reactant at 0.025 *M* each. In the presence of these acids the reaction shows marked deviations from second-order kinetics and is rather too fast for accurate rate measurements. Figure 2 shows % reaction against time in the presence of added perchloric acid at 0.0005 *M* as well as in the absence of any added acid.

Effect of Acetic Acid.—The reaction for methyl acrylate was studied in the presence of added acetic acid at various concentrations. Wright and co-workers observed marked retardation for the methoxy-mercuration of cyclohexene and 2,6-dimethylhepten-5-ol-2 by the addition of acetic acid, the effect increasing with increasing concentrations of acetic acid added. For the methoxy-mercuration of methyl acrylate at 45°, acetic acid exerts absolutely no retarding effect and a slight but definite accelerating effect has been observed (Table II). With 0.012 *M* acetic acid added to 0.025 *M* reactants the rate constant (k) at 45° is found to be 1.54×10^{-1} liter mole^{-1} min.$^{-1}$, as compared with the normal value of 1.35×10^{-1}. With 0.04 *M* acetic acid, the value of k is still higher, 1.63×10^{-1} liter mole^{-1} min.$^{-1}$. The kinetic results are shown in Fig. 2. With relatively high concentrations of added acetic acid, the reaction deviates markedly from second order. It might be expected that as acetic acid accelerates the addition, the reaction ought to be autocatalyzed, since acetic acid is formed as one of the products of the reaction. No such autocatalysis has, however, been observed. Perhaps the amount of acetic acid formed in course of the reaction is too small to exert any appreciable effect. After all, the accelerating effect of acetic acid on the reaction, is, in any case, quite small as shown in Fig. 2.

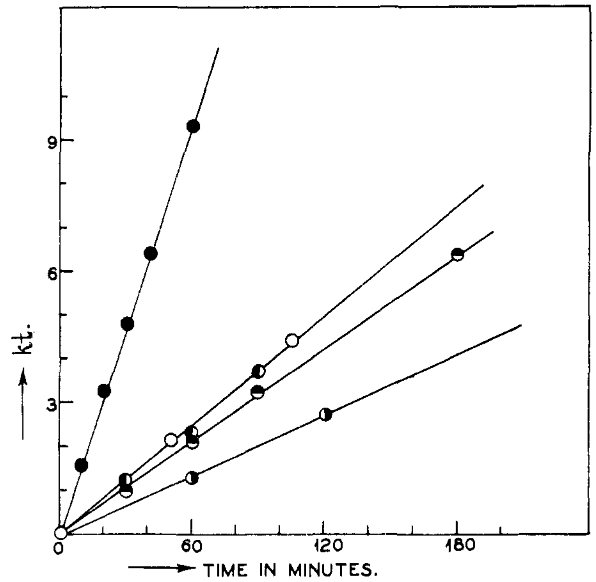

Fig. 3.—Reaction between 0.025 *M* mercuric acetate and 0.025 *M* methyl acrylate with added substances at 45°: ●, 0.012 *M* acetic acid; ◐, 0.0005 *M* sodium acetate; ◑, 0.0125 *M* sodium acetate; ◓, 0.002 *M* sodium acetate; ○, 0.0005 *M* pyridine.

Effect of Acetate and Other Carboxylate Ions.—Added sodium acetate shows a very pronounced retarding effect on the reaction. The effect increases with increasing concentrations of the added sodium acetate but appears to be relatively more pronounced at low than at high concentrations. The effect of sodium acetate has been studied at 45° at three concentrations in the range 0.0005 to 0.0125 *M* using the reactants at 0.025 *M* each. Even with as low as 0.0005 *M* sodium acetate, the rate constant falls down to 0.42×10^{-1} liter mole^{-1} min.$^{-1}$, and with 0.0125 *M* sodium acetate has a value of 0.23×10^{-1} liter mole^{-1} min.$^{-1}$, as compared with the normal value of 1.35×10^{-1}. The results are shown in Table II. Typical kinetic results are presented in Fig. 3. Sodium propionate and butyrate also exert a similar retarding effect on the reaction, which is more or less of the same order as for sodium acetate (Table II). Phenylmercuric acetate also produces an appreciable retardation though the effect is much less pronounced than that of sodium carboxylates.

Effect of Nitrogen Bases.—The effect of nitrogen bases on the reaction rate was also studied, using pyridine and triethanolamine at low concentrations. Only tertiary bases were used, as primary and secondary amines readily add to acrylic esters.

TABLE II

RATE CONSTANTS FOR REACTION BETWEEN METHYL ACRYLATE AND MERCURIC ACETATE (EQUIMOLAR) IN PRESENCE OF ADDED SUBSTANCES AT 45°

Concn. of each reactant (mole per l.)	Concn. of added substances in the reacn. mixture, M		Rate constant $k \times 10$, l. mole^{-1} min.$^{-1}$
0.025	0.012	Acetic acid	1.54
.025	.04	Acetic acid	1.63
.025	.0005	Sodium acetate	0.42
.025	.002	Sodium acetate	.36
.025	.0125	Sodium acetate	.23
.025	.001	Sodium propionate	.40
.025	.005	Sodium propionate	.357
.025	.001	Sodium butyrate	.35
.025	.009	Phenylmercuric acetate	1.06
.025	.01	Phenylmercuric acetate	1.06
.025	.00005	Triethanolamine	0.57
.025	.0005	Triethanolamine	.385
.025	.0005	Pyridine	.42

The nitrogen bases have been found to exert pronounced retardation, the magnitude of the effect being comparable with that of the carboxylates. Thus, with as low as 0.00005 M triethanolamine, the rate constant at 45° falls down to 0.57 $\times 10^{-1}$ liter mole^{-1} min.$^{-1}$. The reaction rates at 45° obtained with various bases at different concentrations are shown in Table II.

Methoxy-mercuration of Ethyl and Butyl Acrylates.—The addition of mercuric acetate to ethyl and butyl acrylates in methanol has been studied at 45° in the same manner as with methyl acrylate. The effects of acetic acid, perchloric acid and of sodium acetate on the reaction rate have been studied, and similar results, namely, slight acceleration with acetic acid, strong acceleration by perchloric acid and strong retardation with sodium acetate have been observed. The normal rate constant at 45° for ethyl acrylate is almost the same as for the methyl ester but for butyl acrylate, the rate constant is somewhat higher. The rate constants for ethyl and butyl acrylates are shown in Table III and IV, respectively.

TABLE III

RATE CONSTANTS FOR REACTION BETWEEN ETHYL ACRYLATE AND MERCURIC ACETATE (EQUIMOLAR) AT 45°

Concn. of each reactant, moles per l.	Concn. of the added substances in the reacn. mixt., M		Rate constant $k \times 10$, l. mole^{-1} min.$^{-1}$
0.025		......	1.35
.0125		......	1.38
.025	0.01	Acetic acid	1.88
.025	.109	Acetic acid	1.99
.025	.0005	Sodium acetate	0.52
.025	.001	Sodium acetate	.40
.025	.04	Sodium acetate	.22
.025	.005	$HClO_4$	Quant. reacn. within 30 min.

TABLE IV

RATE CONSTANTS FOR REACTION BETWEEN BUTYL ACRYLATE AND MERCURIC ACETATE (EQUIMOLAR) AT 45°

Concn. of each reactant, mole per l.	Concn. of the added substances in the reacn. mixt., M		Rate constant $k \times 10$, l. mole^{-1} min.$^{-1}$
0.025	..	....	1.57
.025	..	....	1.57
.025	0.01	Acetic acid	1.70
.025	.10	Acetic acid	1.80
.025	.0005	Sodium acetate	0.42
.025	.005	Sodium acetate	0.35
.025	.005	$HClO_4$	Quant. reacn. within 30 min.

Discussion

Various mechanisms have been suggested for oxy-mercuration of ethylenes. According to Lucas, Hepner and Winstein,[7] the reaction proceeds through an "alkenemercurinium" ion. Wright and co-workers, on the other hand, believe that the addition occurs through a non-ionic mechanism *via* methoxy-mercuric acetate formed by prior solvolysis of mercuric acetate by the alcohol.

Chatt[6] has critically examined the different mechanisms suggested and favors the ionic mechanism. Wright and co-workers, however, have adduced positive evidence in favor of the non-ionic mechanism. If the reaction occurs through prior formation of methoxy-mercuric acetate, addition of acetic acid ought to retard the reaction by suppression of solvolysis. On the other hand, removal of free acetic acid from the solution by some means should accelerate the reaction by promoting further solvolysis. Wright and his co-workers have observed marked retardation for methoxy-mercuration of cyclohexene and of 2,6-dimethylheptene-5-ol-2 by addition of acetic acid. On the other hand, removal of free acetic acid by vacuum distillation from the solution of mercuric acetate results in an acceleration of the reaction rate. If the reaction proceeds through an ionic mechanism, added acetate ions should retard the reaction. Rodgman and Wright[1f] have actually observed marked retardation of the oxy-mercuration of cyclohexene by addition of sodium acetate, but they have attributed this retardation to the formation of disodium tetramercuri-acetate.

In the present case, added acetic acid is absolutely without any retarding effect and, on the contrary, a slight accelerating effect has been observed on adding acetic acid. This observation rules out the solvolysis mechanism, and marked retardation by added sodium acetate lends a strong support to an ionic mechanism. From the results for methyl acrylate presented in Table II, it will be seen that even with 0.0005 M sodium acetate, the reaction rate for 0.025 M reactants at 45° decreases to 0.42 $\times 10^{-1}$ as against the normal average reaction rate of 1.35 $\times 10^{-1}$ l. mole^{-1} min.$^{-1}$. Considering the formation of disodium tetraacetoxy-mercuriacetate, as suggested by Wright, the maximum decrease in the free mercuric acetate concentration that can possibly occur will be to the extent of only 0.00025 M, *i.e.*, 1% of the mercuric acetate taken. The pronounced reduction in the reaction rate cannot, therefore, be attributed to the fall in the free mercuric acetate concentration as a result of mere complex formation. Similar considerations apply to the reactions with ethyl

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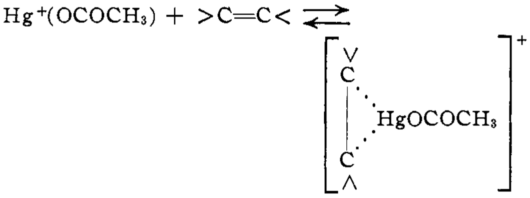
(7) M. J. Lucas, F. R. Hepner and S. Winstein, THIS JOURNAL, **61**, 3102 (1939).

and butyl acrylates. The strong retardation produced even by very small amounts of sodium acetate, and an equally strong retarding effect exerted by propionate and butyrate and also by nitrogen bases in very small concentrations, strongly suggest that the addition proceeds through an ionic mechanism involving a reactive intermediate of the nature of a carbonium ion present in an exceedingly small concentration. Nothing definite can, however, be said about the structure of this carbonium ion, but it seems highly plausible that it is an alkene mercurinium ion, possibly of the type postulated by Lucas, Hepner and Winstein.[7]

It now remains to be seen how an ionic mechanism fits the observed second-order kinetics for the reaction. Mercuric acetate is known to be a very weak electrolyte, so that it is largely present in the solution as neutral molecules, with a very small concentration of acetoxy-mercuric ions formed by dissociation. Further dissociation of the acetoxy-mercuric ion into doubly charged mercuric ion is presumably insignificant. The alkene-mercurinium ion, postulated as the reaction intermediate, may be formed by interaction between a molecule of the unsaturated ester and an acetoxy-mercuric ion, as indicated



$$Hg^+(OCOCH_3) + {>}C{=}C{<} \rightleftarrows \left[\begin{array}{l} >C \\ \;|\;\cdot\cdot\, HgOCOCH_3 \\ <C \end{array}\right]^+ \qquad (1)$$

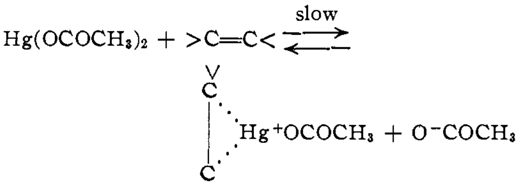
I

The reactive ion I then reacts with the solvent giving the final addition product P

$$I + CH_3OH \longrightarrow P + H^+ \qquad (2)$$

$$H^+ + O^-COCH_3 \rightleftarrows CH_3COOH \qquad (3)$$

Since the degree of dissociation of mercuric acetate is small, the concentration of free acetoxy-mercuric ions at any stage is very nearly proportional to the square root of the total concentration of mercuric acetate, in the absence of any added acetate. The dissociation of acetic acid formed in the course of the reaction is not taken into consideration, which is justified at least for the early stages of the reaction. Hence the over-all reaction should be first order with respect to the unsaturated compound and half order with respect to mercuric acetate, but the observed kinetic results do not conform to this. An ionic mechanism can be compatible with the observed second-order kinetics only if the reactive ion be formed by interaction between molecular, *i.e.*, undissociated, mercuric acetate and the unsaturated compound as indicated.



$$Hg(OCOCH_3)_2 + {>}C{=}C{<} \overset{\text{slow}}{\rightleftarrows} \begin{array}{l} >C \\ \;|\;\cdot\cdot\, Hg^+OCOCH_3 \\ <C \end{array} + O^-COCH_3 \qquad (4)$$

The reaction ion then reacts with the solvent as shown in 2, this reaction being fast. Reaction 4 is then the rate-determining step, and the reaction is clearly first order with respect to each reactant, as observed. The retarding effect of added acetate ion on methoxy-mercuration of acrylic esters can be interpreted with the help of eq. 4 as arising from a decrease in the steady state concentration of the reactive ion. The general retarding effect of bases presumably arises from deactivation of the reactive ion by formation of coördination complexes.

It is yet to be seen whether the catalytic effect of acids on the reaction is in conformity with an ionic mechanism. The accelerating effect of nitric acid, as generally observed for mercuration reactions, has been ascribed by the protagonists of the ionic mechanism to the formation of mercuric nitrate which is more ionizable than the acetate. But the accelerating effect of the strong acids can be neatly interpreted with the help of eq. 4 as arising from the removal of acetate ions and hence increasing the steady state concentration of the reactive ion I. The effect of acetic acid on the reaction rate, however, makes the situation rather difficult. The influence of added sodium acetate shows that the reaction is highly susceptible to the presence of acetate ions even in very small concentrations. So, it might be expected that the addition of acetic acid in relatively high concentrations should generate enough acetate ions so as to exert an appreciable retarding effect on the reaction. The small acceleration by acetic acid may, however, arise as a result of a decrease in the concentration of traces of basic inhibitors present in the solvent, especially the strongly basic methoxy ions formed by autoionization of methanol. Hydrogen ions may also play some active role in the reaction, and the accelerating effect of acids in general may arise from direct catalysis by hydrogen ions.

From the foregoing discussion, it is reasonable to conclude that the addition of mercuric acetate to the double bond in acrylic esters in methanol proceeds through a reactive positive ion. This does not necessarily contradict the conclusions arrived at by Wright and his co-workers about the mechanism of the specific reactions studied by them. It is quite probable that different mechanisms may be operating in oxy-mercuration of different types of unsaturated compounds depending on the nature of the substituents on one or both of the ethylenic carbon atoms.

Acknowledgment.—The authors wish to express their thanks to the Council of Scientific and Industrial Research, India, for financial assistance.