Tetrahedron, 1965, Vol. 21, pp. 457 to 461. Pergamon Press Ltd. Printed in Northern Ireland

METHOXYMERCURATION OF ACRYLONITRILE

A. K. CHAUDHURI and M. N. DAS
Department of Chemistry, Jadavpur University, Calcutta-32, India

(*Received* 19 *May* 1964; *in revised form* 12 *October* 1964)

Abstract—The addition of mercuric acetate to acrylonitrile in methanol has been kinetically studied at 45°. The reaction is greatly accelerated by perchloric acid and appreciably retarded by acetic acid, whereas sodium acetate and nitrogen bases have very little effect on the reaction rate. The mechanism appears to be different from that operating in the reaction with α,β-unsaturated carbonyl compounds. The addition presumably occurs through a non-ionic mechanism involving the prior formation of methoxy-mercuric acetate as the reactive species.

PREVIOUS work[1] from this laboratory indicated that methoxymercuration of acrylic, methacrylic and cinnamic esters and of cinnamaldehyde proceeds through an ionic mechanism, and it was tentatively concluded that possibly an ionic mechanism operates in the oxymercuration of α,β-unsaturated carbonyl compounds in general. It seemed to be of interest to extend the studies to other conjugated systems, e.g. α,β-unsaturated nitriles, to test whether a similar mechanism holds in these cases as well. The present paper reports the results of kinetic studies on methoxy-mercuration of acrylonitrile. Methacrylonitrile and crotononitrile showed practically no signs of reaction under the conditions employed.

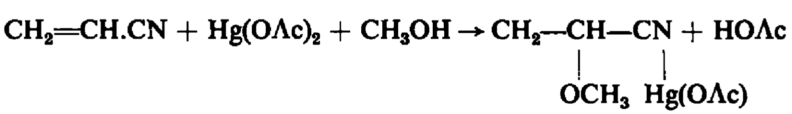
EXPERIMENTAL

Acrylonitrile (Laboratory Reagent, Eastman Kodak) was purified by the usual procedure,[2] only freshly distilled samples being used for kinetic studies.

Measurements were carried out at 45 ± 0·05°. Mercuric acetate was used at concentrations 0·0125–0·025M. The reaction being rather slow, fairly high concentrations of acrylonitrile (0·5 M–2 M) had to be used to obtain measurable rates. The reaction was followed by titrating aliquots of the reaction mixture with standard hydrochloric acid in butanol, using thymol blue as indicator. Experimental details were the same as described earlier.[1a]

RESULTS

The reaction involving the addition of mercuric acetate to acrylonitrile in methanol



$$CH_2{=}CH.CN + Hg(OAc)_2 + CH_3OH \rightarrow \underset{OCH_3}{CH_2}{-}\underset{Hg(OAc)}{CH}{-}CN + HOAc$$

reaches an apparent state of equilibrium, as shown by the fact that when a mixture of acrylonitrile (2 M) and mercuric acetate (0·05 M) is allowed to stand overnight at room temperature, the hydrochloric acid titre indicates about 70% reaction, after which the titre value does not change to any appreciable extent. The reverse reaction, if any, should not, however, assume much importance during the initial stages of the reaction.

[1a] K. L. Mallik and M. N. Das, *J. Amer. Chem. Soc.* **82**, 4269 (1960);
[b] A. K. Chaudhuri, K. L. Mallik and M. N. Das, *Tetrahedron* **19**, 1981 (1963).
[2] J. C. Bevington and D. E. Eaves, *Trans. Farad. Soc.* **55**, 1777 (1959).

Rates were studied upto a maximum period of 3 hr during which the reaction proceeds smoothly, being apparently free from complications.

The acrylonitrile concentration used being much higher than that of mercuric acetate, the reaction is virtually zero order in the olefin and was found to be first order in mercuric acetate. The first order rate constant was found to be very nearly proportional to the acrylonitrile concentration, which indicates first order kinetics with respect to the olefin as well. The mean value of the second order rate constant, k at 45°, based on the results of nineteen independent runs, was obtained as $(1{\cdot}56 \pm 0{\cdot}065) \times 10^{-3}$ litre-mole^{-1} min^{-1}. The rate of methoxymercuration of acrylonitrile thus appears to be nearly one hundred times slower than the reaction with acrylic esters at the same temperature.[1a]

TABLE 1. RATE CONSTANTS k FOR REACTION BETWEEN ACRYLONITRILE (1·0M) AND MERCURIC ACETATE (0·025M) AT 45°

Concentration of added substance in reaction mixture	$k \times 10^3$ lit mole^{-1} min^{-1}
None	1·56 ± 0·06[a]
0·04 Acetic acid	0·99
0·10 Acetic acid	0·87
0·0005M Sodium acetate	1·68
0·001M Sodium acetate	1·85
0·005M Sodium acetate	1·67
0·02M Sodium acetate	1·61
0·04M Sodium acetate	1·61
0·0005M Triethanolamine	1·71
0·0005M Pyridine	1·70
0·001M Pyridine	1·80

[a] Mean of fourteen values obtained from separate runs.

Reaction in the presence of added substance. The reaction was studied in the presence of perchloric acid, acetic acid, sodium acetate and tertiary nitrogen bases like pyridine and triethanolamine. For all the runs carried out to test the effects of these added substances, the initial concentrations of acrylonitrile and mercuric acetate were 1·0M and 0·025M respectively. Most of the runs were carried out in duplicate, and the mean values of rate constants calculated from the early stages of the reaction are shown in Table 1.

Effect of perchloric acid. The reaction was found to be greatly accelerated by perchloric acid, and with 0·04M acid in the reaction mixture, about 95% reaction was observed within 75 min, whereas in the absence of the acid, only 20% reaction occurs in 3 hr. The catalysed reaction is obviously too fast for kinetic measurement by the method employed. It should be noted that the uncatalysed reaction seemingly reaches a state of equilibrium, but in the presence of perchloric acid nearly quantitative reaction is observed. A similar observation was also made for the reaction with acrylic and methacrylic esters.[1]

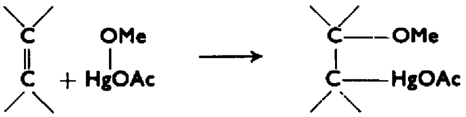
Effect of added acetic acid. Definite retardation of the reaction was noted in the presence of acetic acid. Thus, with 0·04M acetic acid, the rate constant is 0·99 × 10^{-3} litre-mole^{-1} min^{-1} and the value decreases to 0·87 × 10^{-3} with 0·1M acetic acid (Table 1). About 17% mercuric acetate is added in 120 min in the absence of added acetic acid, whereas with 0·04M and 0·1M acetic acid in the reaction mixture, addition amounts to nearly 12% and 10% respectively during the same period under otherwise identical conditions.

Effect of acetate and nitrogen bases. The concentration of sodium acetate in the reaction mixture was varied from 0·0005M to 0·04M, but in no case was any marked change in the reaction rate noticed. The effects of pyridine and triethanolamine are similar (Table 1). Some values of the rate constants suggest a tendency towards slightly higher reaction rates, but in view of the considerable spread (±4%) in the values of rate constants observed for the normal reaction, this difference is too small to be taken into account. The only definite conclusion to be drawn from the results is that neither sodium acetate nor the nitrogen bases have a retarding effect which is pronounced in the case of α,β-unsaturated esters.[1]

DISCUSSION

Two different mechanisms have been found to operate in the oxymercuration of different types of olefinic compounds. Lucas *et al.*[3] suggest that the reaction proceeds through an "alkenemercurinium ion" as the reactive intermediate. The results obtained by Wright *et al.*[4] for the methoxymercuration of cyclohexene and 2,6-dimethylhept-5-en-2-ol are, however, incompatible with such a mechanism and they conclude that the reaction occurs through molecular addition of methoxymercuric acetate (MeOHgOAc) formed by prior solvolysis of mercuric acetate by the alcohol, as shown below.

$$\mathrm{Hg(OAc)_2 + MeOH \rightleftharpoons MeOHgOAc + HOAc} \qquad (1)$$



(2)

On the other hand, results obtained in this laboratory for methoxymercuration of several α,β-unsaturated esters and of cinnamaldehyde indicate that the reaction in these cases presumably proceeds through an ionic mechanism involving a cation as the reactive intermediate formed by interaction between mercuric acetate and the olefinic compound. Possibly the cation formed is of the type of an alkenemercurinium ion which rapidly reacts with a methoxy ion (derived from self-ionization of methanol) giving the final product.

The unsaturated carbonyl compounds studied earlier, indicate that the addition is (i) greatly accelerated by perchloric acid, (ii) appreciably *accelerated* by acetic acid and (iii) *strongly retarded* by sodium acetate and nitrogen bases. These observations, especially (ii) and (iii), can be satisfactorily correlated with a mechanism represented

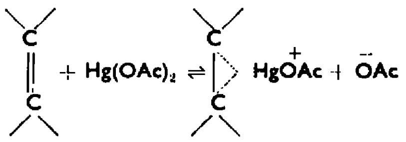
---

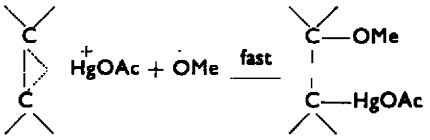
[3] M. J. Lucas, F. R. Hepner and S. Winstein, *J. Amer. Chem. Soc.* **61**, 3102 (1939).

[4a] J. Romeyn and G. F. Wright, *J. Amer. Chem. Soc.* **69**, 697 (1947);

[b] A. G. Brooks, A. Rodgman and G. F. Wright, *J. Org. Chem.* **17**, 988 (1952);

[c] A. Rodgman and G. F. Wright, *Ibid* **18**, 1617 (1953).


(3)


(4)

by Eqs (3) and (4). It may be noted that Wright *et al.*[5] favour a similar mechanism for the oxymercuration of norbornene.

In the present case, however, such a mechanism does not appear to be in conformity with the kinetic results obtained for the methoxymercuration of acrylonitrile. The salient features of this reaction, as reported in the previous section, are that the addition is (i) greatly accelerated by perchloric acid, (ii) appreciably *retarded* by acetic acid and (iii) very slightly accelerated, *practically unaffected*, by the bases.

The mechanism of methoxymercuration of acrylonitrile thus appears to be different from that operating in the reaction with the carbonyl compounds. The kinetic results strongly suggest that the reaction mechanism here presumably involves prior formation of methoxymercuric acetate by solvolysis, as represented by Eqs. (1) and (2) above.

Added acetic acid should suppress the solvolysis of mercuric acetate (Eq. 1), thus decreasing the equilibrium concentration of methoxymercuric acetate which is presumed to be the reactive species. Hence, the reaction ought to be retarded by acetic acid as actually observed. For an ionic mechanism represented by Eqs 3 and 4, there is no reason why an appreciable retardation should occur with a small amount of added acid which hardly produces any change in the medium.

The absence of any retarding effect of added acetate (and nitrogen bases) is also quite significant, ruling out the possibility of a mechanism involving an alkenemercurinium ion. The very slight acceleration noticed in the presence of added bases may perhaps be attributed to an increase in the concentration methoxymercuric acetate as a result of a slight shifting of the equilibrium (1) towards the forward direction. The observed effect, however, is quite small and this point cannot be emphasized strongly enough.

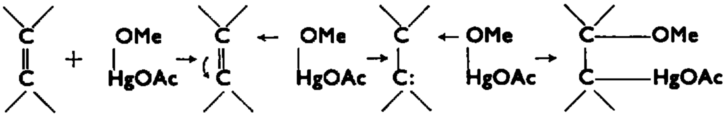
The tremendous acceleration produced by perchloric acid is the only feature common to the reactions with acrylonitrile and the α,β-unsaturated compounds studied earlier. Wright *et al.*[5] who found that the oxymercuration of norbornenes is catalysed by strong acids, consider this (acid-catalysis) as a criterion of the ionic mechanism, described above. In the present case, however, the observed effects of added acetic acid and acetate are clearly incompatible with such a mechanism. The accelerating effect of perchloric acid may well arise from a greater tendency on the part of mercuric perchlorate to undergo solvolysis, as compared with the acetate.

If it be accepted that methoxymercuric acetate is the active species which adds to the carbon-carbon double bond in acrylonitrile, the next pertinent question arises as to the mode of this addition, i.e. whether the mechanism operating at this stage is

---

[5] M. J. Abercrombie, A. Rodgman, K. R. Bharucha and G. F. Wright, *Canad. J. Chem.* 37, 1328 (1959).

homolytic or heterolytic. It has been suggested by Wright[6] that methoxymercuric acetate adds molecularly to the double bond, which for the present case may be shown as:



(5)

The oxygen atom in the methoxy group is supposed to lead the attack which in the case of acrylonitrile must be on the β-carbon atom, as shown. It may be recalled that neither α-methyl nor β-methyl acrylonitrile shows any sign of adding mercuric acetate in methanol. This presumably indicates that either the inductive effect of the methyl group inhibits the addition of MeOHgOAc which here acts as a nucleophile (via methoxy group) or steric factors are playing a dominant role in the addition. Results obtained so far do not, however, furnish any clue to further details of the mechanism of addition.

This much is clear, however, that acrylonitrile, a typical α,β-unsaturated nitrile, behaves in a manner different from α,β-unsaturated carbonyl compounds with regard to the mechanism for methoxymercuration. This difference may perhaps be traced to a difference in the electron distribution in the two conjugated systems:

$$\mathrm{C{=}C{-}C{=}O} \text{ and } \mathrm{C{=}C{-}C{\equiv}N}.$$

This difference is also reflected in the values of the dipole moments of α,β-unsaturated nitriles and carbonyl compounds, as compared with those for the corresponding saturated compounds.[7]

[6a] G. F. Wright, *Chem. Canad.* **2**, 29 (1950).

[b] J. Chatt, *Chem. Revs.* **48**, 7 (1951).

[7a] E. C. Hurdis and C. P. Smyth, *J. Amer. Chem. Soc.* **65**, 89 (1943);

[b] C. P. Smyth, *Dielectric Behaviour and Structure* p. 282. McGraw-Hill (1955).