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The Initial Mechanism of Vinyl Acetate Synthesis from Acetic Acid and Acetylene Catalyzed by Active Carbon–Zinc Acetate

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The initial product of the reaction of CD_3COOH and C_2H_2 catalyzed by an active carbon-$Zn(OAc)_2$ catalyst at 185°C was 100% nondeuterated vinyl acetate, $CH_2CHCO_2CH_3$. We postulate that adsorbed acetylene forms a σ as opposed to a π-bonded complex with the zinc acetate catalyst and that the initial sequence leading to vinyl acetate is the following (where HOAc* = CD_3COOH):

$$\begin{aligned}
&C_2H_2 + Zn(OAc)_2 && \rightarrow \overset{+}{C}H{=}CH{-}\overset{-}{Zn}(OAc)_2 \\
&\overset{+}{C}H{=}CH{-}\overset{-}{Zn}(OAc)_2 && \rightarrow AcOCH{=}CH{-}ZnOAc \\
&AcOCH{=}CH{-}ZnOAc + HOAc^* && \rightarrow AcOCH{=}CH_2 + ZnOAcOAc^*
\end{aligned}$$

INTRODUCTION

The preparation of vinyl acetate from acetylene and acetic acid catalyzed by zinc acetate on active carbon is a well-established process (personal communication, Ref. (*1*)) and is represented stoichiometrically by

$$C_2H_2 + CH_3COOH \rightarrow CH_3COOCHCH_2$$

The reaction is usually carried out near 180–210°C at a total pressure slightly above 1 atm and with a two- to sevenfold excess of acetylene. However, in spite of much study, almost nothing is known of the mechanism of the reaction or of the role played at the molecular level by this two-component catalyst system. The kinetics of this reaction have been studied many times (*1–4*) and a discussion of current views of the mechanism have recently been given by Prasad *et al.* (*2*). The kinetic data will be reviewed below. This paper is concerned with a study of this reaction using deuterated acetic acid, CD_3COOH. As will be shown, results allow us to unambiguously deduce the initial mechanism of the reaction.

EXPERIMENTAL

Our studies were carried out using a standard stainless-steel microreactor which had provision for vaporizing HOAc and mixing this with C_2H_2 at a C_2H_2/HOAc mole ratio of 7/1. The cylindrical reactor (21 mm diam × 140 mm) was packed with a homogeneous mixture of 10 g of catalyst and 60 g of glass beads (diam 6 mm) and the total pressure in the reaction was 1.2 atm. Liquid acetic acid was injected into the vaporizer at a rate of 0.2 mol/h using a syringe. The catalyst was prepared from Chemviron active carbon (Pittsburgh Activated Carbons, surface = 1200 m^2g^{-1}) by solution impregnation; the resultant dried catalyst contained 28.5% $Zn(OAc)_2$.

Product analysis was carried out using an A.E.I. MS 20 mass spectrometer which, with its continuously pumped inlet system, was situated just after the reactor. With the reactor empty the mass spectrum of acetic acid could be detected 30 s after it entered the vaporizer. In a normal run the mass spectrum of the parent ion peaks of CH_3COOH (HOAc) at 60, CD_3COOH (HOAc*) at 63, $CH_3COOCHCH_2$ (VA) at

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86, and $CD_3COOCHCH_2$ (VA*) at 89 were scanned about every 45 s, or every 15 s in the 86–89 region alone. Under steady-state conditions the conversion of HOAc to VA was about 12% (GC analysis) and the ratio of the MS parent ion intensities of acetylene (M = 26), acetic acid (M = 60), and vinyl acetate (M = 86) was 400 : 10 : 1.

Deuterated acetic acid (>99% CD_3COOD) was purchased from Centre d'Etudes Nucléaires (Saclay, France) or from Merck Isotopes Inc. (Montreal, Canada). No precaution was taken to prevent exchange of the acidic proton during filling of the syringe and, as will be explained below, the experiments were essentially carried out using CD_3COOH.

RESULTS

The following experimental procedure was used in all cases. After charging the reactor with the catalyst, the normal flow of C_2H_2 was started (or N_2 in the case of the exchange studies with the catalyst) and the reactor temperature was raised to 185°C. Then liquid acetic acid was injected into the vaporizer/mixer which was at 120°C and was just upstream from the reactor. A typical curve showing the growth of the MS signals due to acetic acid and vinyl acetate as a function of time ($t = 0$ is when acetic acid enters the vaporizer) is shown in Fig. 1. Note that VA was detected after 30 s (the same delay as for HOAc using an empty reactor) and before acetic acid. Steady state was only reached after about 16 min and the maximum in the VA signal after about 5 min corresponded approximately to the maximum rise in temperature in the reactor, to about 191°C, due to the liberated heat of reaction, and the temperature only returned to 185°C after about 16 min.

The initial acetic acid detected in exchange or VA production experiments using CD_3COOD was only about 10% deuterated at the acidic "hydrogen," regardless of whether the methyl group was CH_3 or CD_3. This was also true if the reactor was empty, in which case the methyl was 100% CD_3. The exact percent acidic D varied by ±3% from experiment to experiment, but for a given experiment it was constant during the first 10 min; thereafter it slowly increased and in one experiment, was about 25% after 30 min. In experiments which produced vinyl acetate (OAc or OAc*), the percentage C_2H_2D–acetate was also constant at about 5% during the first 10 min. Therefore, we conclude that H^+ exchange with DOAc* occurred mainly as a result of exposure of the latter to air and the apparatus each day. (The apparatus was exposed to air for at least 18 h between all experiments.) In effect, our experiments during the first 10 min were carried out using a constant HOAc*/DOAc* mixture (ratio ~ 10 : 1) and in subsequent discussion the words "exchange" or "deuterated" only refers to the methyl group in the acetate.

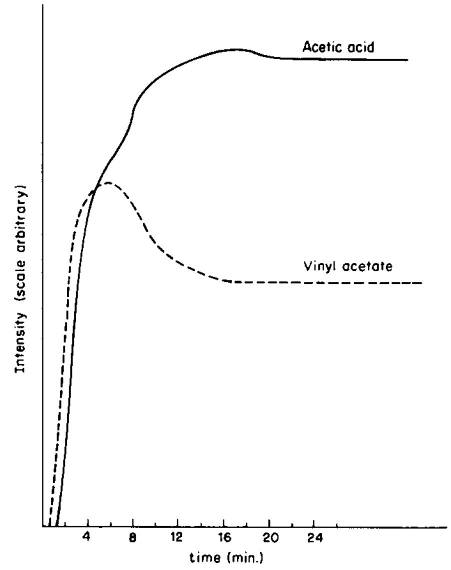


FIG. 1. Growth of the mass spectrometer signal for acetic acid (HOAc) and vinyl acetate (VA) as a function of time. Zero time is when HOAc reaches the vaporizer. The intensity scale is arbitrary and does not give the relative concentrations of HOAc and VA.

Deuterated acetic acid did not exchange with the active carbon alone. As expected (*5*) it did exchange with $Zn(OAc)_2$ on the active carbon catalyst and a typical plot showing the time evolution of the MS signals for CH_3COOH and CD_3COOH when a

7/1 mixture of N_2/CD_3COOH was passed over this catalyst is shown in Fig. 2. Note that in the first 3 min the mixture is CD_3COOH rich.

Some curves showing the time evolution of VA and VA* for the reaction between HOAc* and C_2H_2 over active carbon/$Zn(OAc)_2$ are presented in Fig. 3. It is apparent that the initial product is 100% undeuterated vinyl acetate, although with time this eventually became 100% VA*. In the case of the isotopically reversed reaction, that is, using HOAc with a 100% deuterated $Zn(OAc^*)_2$/carbon catalyst, curves similar to those shown in Fig. 3 were obtained, with the labels reversed, and the initial product was 100% VA*.

DISCUSSION

The kinetics of this reaction have been studied many times (*1*–*5*) and there is a consensus that, near 180°C and with excess C_2H_2, the reaction is first-order in C_2H_2 pressure. However, at higher HOAc partial pressures, the latter inhibits the reaction and the rate law takes the form

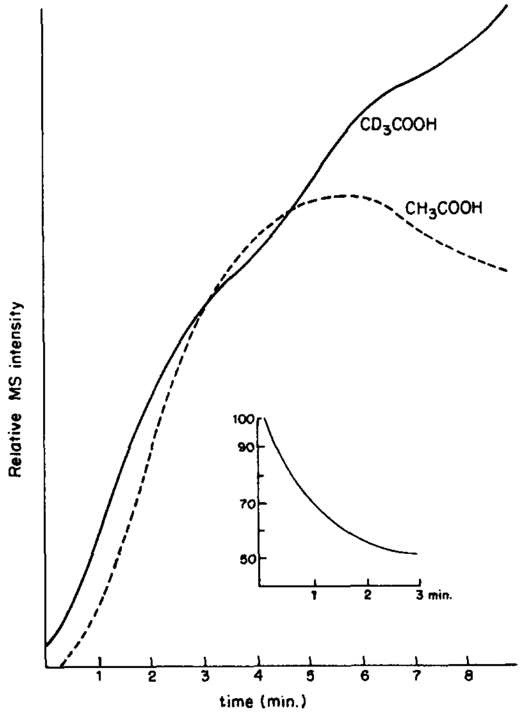


FIG. 2. Time evolution of CD_3COOH and CH_3COOH when a N_2/CD_3COOH mixture (7/1) passes over an active carbon–$Zn(CH_3COO)_2$ catalyst at 185°C. Inset shows the CD_3COOH percentage in the first 3 min.

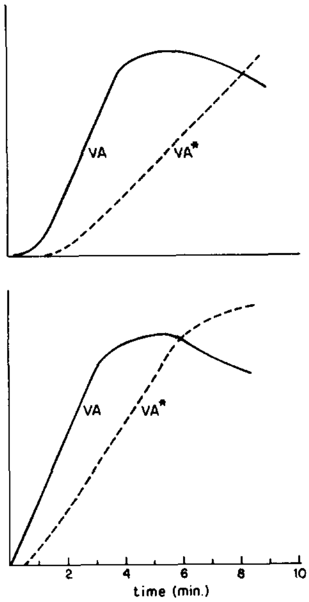


FIG. 3. Curves from two experiments showing the evolution of VA* ($CD_3COOC_2H_3$) and VA ($CH_3COOC_2H_3$) as a function of time when passing a mixture of C_2H_2/CD_3COOH (7/1) over the catalyst at 185°C. The ordinate gives the relative intensities.

$$r = k\frac{[C_2H_2]}{1 + K[HOAc]}$$

where $[x]$ denotes the pressure of x. One possible mechanism is (*1*):

$$Zn(OAc)_2 + C_2H_2 \xrightarrow[slow]{k} Zn(OAc)_2C_2H_2 \quad (1)$$

$$Zn(OAc)_2C_2H_2 + HOAc \xrightarrow{fast} Zn(OAc)_2 + CH_2CHOAc \quad (2)$$

with competition for sites from the equilibrium

$$Zn(OAc)_2 + HOAc \overset{K}{\rightleftharpoons} Zn(OAc)_3H \quad (3)$$

However, a similar rate law can be derived if it is assumed that the adsorption of C_2H_2 on the "complex" in Reaction (3) is the rate-limiting step,

$$\mathrm{Zn(OAc)_3H + C_2H_2 \xrightarrow[\text{slow}]{k'} Zn(OAc)_3HC_2H_2} \quad (4)$$

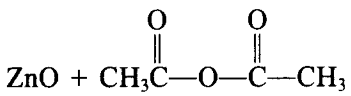
$$\mathrm{Zn(OAc)_3HC_2H_2 \xrightarrow{\text{fast}} Zn(OAc)_2 + CH_2CHOAc} \quad (5)$$

with competition

$$\mathrm{Zn(OAc)_3H + HOAc \overset{K'}{\rightleftharpoons} Zn(OAc)_4H_2} \quad (6)$$

More recent work by Cornelissen *et al.* (*4*), Goyal *et al.* (*3*), and Prasad *et al.* (*2*) have shown that the rate law is probably more complicated and that the rate may also be inhibited by competition for sites by adsorbed VA. Prasad *et al.* (*2*) have also pointed out that decomposition and regeneration of the catalyst near 180–200°C must also be considered.

$$\mathrm{Zn(OAc)_2 \rightarrow}$$



$$\mathrm{ZnO + CH_3\overset{\overset{O}{\|}}{C}\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3} \quad (7)$$

$$\mathrm{ZnO + 2HOAc \rightarrow Zn(OAc)_2 + H_2O} \quad (8)$$

They assumed that the rate of reaction (8) (and therefore the rate of change of catalyst concentration) would be controlled by the adsorption of HOAc, whereas that of VA production by the adsorption of C_2H_2. Their experimental data showed that reactions (7) and (8) were relatively important at 190°C, but less important at 170–180°C.

While kinetic studies may give some insight into the reaction mechanism, they cannot usually provide structural information at the molecular level. Active carbon alone or zinc acetate alone are inactive and it is apparent that the role of the carbon goes beyond merely providing a medium for dispersing the $Zn(OAc)_2$ (*1, 4, 6*). Various authors have suggested that the carbon can donate electrons to the zinc (*1, 6–8*) and that this somehow promotes the adsorption of acetylene. If, in Reactions (1)–(3), step (2) involves a reaction between adsorbed acetylene (σ or π bonded) and gaseous acetic acid, then the initial product using HOAc* would be 100% VA* (neglecting HOAc*/$Zn(OAc)_2$ exchange) and should continue to be 100% VA*. However, with Reactions (4)–(6), and assuming that the acidic proton is labile such that the three acetate groups are equivalent as suggested by Siling and Gelbshtein (*9*), the initial complex using HOAc* would be $Zn(OAc)_2(OAc^*)HC_2H_2$ and on a statistical basis the initially produced VA should be C_2H_3OAc and $C_2H_3OAc^*$ in the ratio 2 : 1 which with time would approach 100% $C_2H_3OAc^*$. Finally, if we have a specific σ complex between the catalyst and acetylene, we could envisage the sequence

$$\mathrm{\overset{+}{C}H\text{=}CH\text{—}\overset{-}{Zn}(OAc)_2 \rightarrow AcO\text{—}CH\text{=}CH\text{—}ZnOAc} \quad (9)$$

$$\mathrm{AcOCH\text{=}CH\text{—}ZnOAc + HOAc^* \rightarrow AcOCH\text{=}CH_2 + ZnOAcOAc^*} \quad (10)$$

in which the initial product using 100% HOAc* as a reactant would be 100% VA. With time this will, of course, eventually become 100% VA*.

The above serves to show how diverse may be our expectations for the initial VA/VA* ratio and other intermediate cases are possible. In view of the simultaneous HOAc/$Zn(OAc)_2$ exchange reaction which is reported to have a half-life of 1 h at 150°C (*5*), it is apparent that any experimental result which showed that a mixture of VA and VA* (or only VA*) when using 100% HOAc* as a reactant would be difficult to interpret. However, the results conclusively show that the initial product VA exclusively contains the isotopically marked acetate which is initially present in the catalyst and is not that from the reactant acetic acid. Figure 2 shows that even after 30 s exposure for the exchange reaction, the gas phase is still 80% HOAc*, whereas the vinyl acetate product after the same time interval is 90% unlabeled. It is solely due to this fortuitous set of circumstances that we can be so definitive in stating that we believe that the mechanism of vinyl acetate synthesis in the initial stages must involve steps (1), (9), and (10). It certainly does not involve an interaction between adsorbed C_2H_2 and gas-phase acetic acid.

We stress that our conclusions only apply to the initial mechanism of reaction since, with our apparatus, exchange is well under way by the time (16 min) steady state has been established. We also believe that it would be difficult to study this reaction by suddenly switching from an HOAc flow to an HOAc* flow at steady state since separate experiments have shown that after stopping the acetic acid flow to the vaporizer there is a delay of about 5 min before there is a decay of the acetic acid signal. Since the decay occurs after about 30 s with an empty reactor, we assume that much acetic acid is adsorbed on the catalyst.

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