# The Reaction of Acrolein with Acetylperoxyl Radicals in the Gas-Phase

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ABSTRACT: A rate constant for the epoxidation of acrolein by acetylperoxyl radicals has been determined to be  $k_4 = (1.3 \pm 0.9) \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  at 383 K, which is anomalously fast in comparison with the epoxidation of alkenes. Abstraction of the acyl hydrogen atom from acrolein by acetylperoxyl radicals at 393 K was found to be at least 60 times slower than from acetaldehyde and at least three orders of magnitude slower than abstraction of the acyl hydrogen atom from of the epoxide of acrolein. The fast rate for epoxidation of acrolein and the slow rate for hydrogen abstraction provide an explanation for the anomalously slow rate for the autoxidation of acrolein and suggests that acrolein formed during the autoxidation of alkene will react further to give its epoxide, and not exclusively by abstraction of the acyl hydrogen atom as was previously accepted. © 1999 John Wiley & Sons, Inc., Int J Chem Kinet 31: 277–282, 1999

## INTRODUCTION

The gas-phase autoxidation of propene has been much studied recently, with detailed reaction mechanisms being produced [1-3] to be used as submechanisms in the simulation of hydrocarbon combustion [4] and to study the possible production of propene oxide via propene autoxidation [5].

Although at lower temperatures the majority of the propene reacts by radical addition to the double bond to yield either the epoxide or acetaldehyde and formaldehyde, hydrogen abstraction can occur under all conditions. The resulting allyl radical can yield acrolein, and computer simulations have suggested that the subsequent behavior of the unsaturated aldehyde can play a significant role in the autoxidation of propene. For example, during the simulation of the oxidation of a fuel-rich propene:oxygen mixture at 550 K, ca. 40% of the epoxide formed was predicted to be produced by epoxidation of the alkene by the acrylperoxyl radical (reaction 3) [3], which is formed by hydrogen

Correspondence to: M. S. Stark © 1999 John Wiley & Sons, Inc. atom abstraction from acrolein (reaction 1), followed by oxygen addition (reaction 2):

$$C_2H_3CHO + X \cdot \longrightarrow \cdot C_2H_3CO + XH$$
 (1)

$$C_2H_3CO + O_2 \longrightarrow C_2H_3C(O)O_2$$
 (2)

$$C_{2}H_{3}C(O)O_{2} \cdot + C_{3}H_{6} \longrightarrow \cdot C_{2}H_{3} + CO_{2} + C_{3}H_{6}O \quad (3)$$

Mechanisms describing the further reaction of acrolein have tended to assume that attack on the carboncarbon double bond was insignificant, with hydrogen atom abstraction from the aldehyde group dominating [1-3], and with the subsequent mechanism and reaction rates chosen by assuming analogous behavior to that of acetaldehyde, which has been more thoroughly studied [6].

However, it is possible that the assumption of the lack of reactivity of the C=C double bond is not valid. In this work, two reactions of acylperoxyl radicals with acrolein have been examined, namely the epoxidation of the C=C double bond (reaction 4) and abstraction of the acyl hydrogen atom (reaction 5) by acetylperoxyl radicals:

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$$CH_{3}C(O)O_{2} \cdot + C_{2}H_{3}CHO \longrightarrow CH_{3} + CO_{2} + H_{2}\overrightarrow{COCHCHO}$$
(4)

$$\begin{array}{c} CH_{3}C(O)O_{2} \cdot + C_{2}H_{3}CHO \longrightarrow \\ CH_{3}C(O)O_{2}H + C_{2}H_{3}\dot{C}O \quad (5) \end{array}$$

The consequences of these findings on the reactions of acrolein during the autoxidation of propene are discussed.

#### **EXPERIMENTAL**

Acrolein was distilled and dried over calcium hydride. Acetaldehyde (Aldrich) was distilled and stored over molecular sieve. Oxygen, helium (B.O.C.), 1-butene, and propanal (Aldrich) were used without further purification. The surface of the reaction vessel (Pyrex, volume =  $167 \text{ cm}^3$ , surface : volume ratio = 1.00cm<sup>-1</sup>) was conditioned by performing repeated autoxidation experiments until a reproducible overall rate for the autoxidation of acetaldehyde was obtained. Analysis was mainly by GC (Pye PU4500) with a Tenax GC column and flame ionization detector (2.5 m length, 3 mm i.d.). Product identification was by GC-mass spectrometry (VG Analytical Autospec, electron impact, 6 kV). The concentrations of products were calibrated using authentic samples (Aldrich), except for the epoxide of acrolein, glycidaldehyde, and peracetic acid. The peracid was determined by allowing some of the reacted gases to flow into an evacuated vessel, where they were dissolved in water, followed by titration with potassium iodide [7]. Glycidaldehyde was prepared by the addition of hydrogen peroxide to an aqueous solution of acrolein [7,8]. A pure sample could not be extracted however, so its calibration factor was assumed to be the same as methylglyoxal, as it is known that isomeric epoxide and ketone groups have very similar FID calibration constants [9]. For example, with the FID that was used, the calibration constants for acetone and propene oxide differed by less than the experimental error of a few percent.

### **RESULTS AND DISCUSSION**

Mixtures of acetaldehyde and oxygen with smaller amounts of acrolein were reacted together at 393 K (Fig. 1). During the initial stages of its autoxidation, acetaldehyde is consumed by abstraction of the acyl hydrogen atom by the dominant radical present, the acetylperoxyl radical (reaction 6) [10]:



Figure 1 Consumption of acetaldehyde ( $\bigcirc$ ) and acrolein (+) during their co-oxidation: initial concentrations, [CH<sub>3</sub>CHO]/[O<sub>2</sub>]/[He]/[C<sub>2</sub>H<sub>3</sub>CHO] = 5/5/4/1; total initial pressure, 400 mbar; 393 K.

$$\begin{array}{rcl} CH_{3}C(O)O_{2} \cdot &+ CH_{3}CHO \longrightarrow \\ CH_{3}C(O)O_{2}H &+ CH_{3}\dot{C}O & (6) \end{array}$$

with a rate constant of  $k_6 = 1.7 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  $exp(-30.1 \text{ kJ mol}^{-1}/\text{RT})$ . There is an estimated standard error for the rate constant of ca.  $\pm 65\%$  at 393 K [11]. During the co-oxidation of acetaldehyde and acrolein, the acrolein is sufficiently unreactive that it is unlikely to be a major perturbation to the oxidation of the acetaldehyde, so the dominant radical will still be acetylperoxyl. Therefore any acrolein that does react will do so predominantly with acetylperoxyl radicals formed by the oxidation of acetaldehyde. As acrolein does not noticeably react away in Figure 1, an upper bound for the ratio of the rate constants for abstraction from acrolein and acetaldehyde  $(k_5/k_6)$  can be estimated from the rate of consumption of acetaldehyde and the upper limit for the rate of removal of acrolein:

 $k_{5}/k_{6}(393 \text{ K}) = \frac{(d[C_{2}H_{3}CHO]/dt)_{\text{initial}}[CH_{3}CHO]_{\text{initial}}}{(d[CH_{3}CHO]/dt)_{\text{initial}}[C_{2}H_{3}CHO]_{\text{initial}}} < 0.017 \quad \text{(I)}$  $k_{5}(393 \text{ K}) < 2.9 \times 10^{3} \text{ dm}^{3}\text{mol}^{-1}\text{s}^{-1}$ 

As a comparison, acetaldehyde and propanal were co-oxidised under the same conditions, the propanal reacts away faster than acetaldehyde (Fig. 2), with  $k_7/k_6(393 \text{ K}) = 2.5 \pm 0.3$ , demonstrating that the presence of the conjugated vinyl group instead of an ethyl group reduces the rate of hydrogen atom abstraction



**Figure 2** Consumption of acetaldehyde ( $\bigcirc$ ) and propanal (+) during their co-oxidation: initial concentrations, [CH<sub>3</sub>CHO]/[O<sub>2</sub>]/[He]/[C<sub>2</sub>H<sub>5</sub>CHO] = 5/5/4/1; total initial pressure, 400 mbar; 393 K.

from the acyl group by a factor of at least  $\times 125$  at 393 K:

$$CH_{3}C(O)O_{2} \cdot + C_{2}H_{5}CHO \longrightarrow$$

$$CH_{3}C(O)O_{2}H + C_{2}H_{5}\dot{C}O \qquad (7)$$

 $k_7(393 \text{ K}) = (4.3 \pm 2.8) \times 10^5 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ 

The build up of the products glycidaldehyde and peracetic acid produced during the co-oxidation of acrolein and acetaldehyde are given in Figure 3. The epoxide, which is only formed in small quantities, is far more reactive than acrolein itself. Its concentration decreases when that of peracetic acid becomes significant, suggesting its consumption by addition to the peracid to form glycidaldehyde monoperacetate, which would decompose at this temperature to two acid molecules (reaction 8). This reaction is analogous with that of peracetic acid with acetaldehyde, which is known to be a major source of the large quantities of acetic acid produced during acetaldehyde autoxidation at these temperatures [12,13].

$$CH_{3}C(O)O_{2}H + H_{2}COCHCHO \Longrightarrow$$

$$H_{2}COCHCH(OH)O_{2}C(O)CH_{3} \longrightarrow CH_{3}C(O)OH$$

$$+ H_{2}COCHC(O)OH \quad (8)$$

That the epoxide increases in concentration early in the reaction when the peracid concentration is low suggests that the formation of the epoxide by the reaction of acrolein with the peracid is minor (the partial pressure of the peracid for the early part of the reaction was lower than the detection limit of ca. 2 mbar).



**Figure 3** Production of peracetic acid ( $\bigcirc$ ) and glycidaldehyde ( $\times$ 100) (+) during the co-oxidation of acetaldehyde and acrolein: initial concentrations, [CH<sub>3</sub>CHO]/[O<sub>2</sub>]/[He]/ [C<sub>2</sub>H<sub>3</sub>CHO] = 5/5/4/1; total initial pressure, 400 mbar; 393 K.

To obtain a rate constant for the epoxidation of acrolein by peracetyl radicals ( $k_4$ ), small quantities of acrolein and 1-butene were co-oxidized with acetal-dehyde (Fig. 4), the ratio of the rate of build up of the two epoxides allowed the determination of the ratio of the rate constants ( $k_4/k_9$ ) for their formation at 383 K:

$$CH_{3}C(O)O_{2} \cdot + 1 - C_{4}H_{8} \longrightarrow$$

$$CH_{3} \cdot + CO_{2} + H_{2}OOCHC_{2}H_{5} \quad (9)$$



**Figure 4** Production of glycidaldehyde (+) and 1-butene oxide ( $\bigcirc$ ) during the co-oxidation of acetaldehyde, 1-butene and acrolein: initial concentrations, [CH<sub>3</sub>CHO]/[O<sub>2</sub>]/[He]/[C<sub>2</sub>H<sub>3</sub>CHO]/[1-C<sub>4</sub>H<sub>8</sub>] = 10/10/8/1/1; total initial pressure, 400 mbar; 383 K.



**Figure 5** Production of glycidaldehyde (+) and 1-butene oxide ( $\bigcirc$ ) during the co-oxidation of acetaldehyde, 1-butene and acrolein: initial concentrations, [CH<sub>3</sub>CHO]/[O<sub>2</sub>]/[He]/[C<sub>2</sub>H<sub>3</sub>CHO]/[1-C<sub>4</sub>H<sub>8</sub>] = 10/10/8/1/1; total initial pressure, 400 mbar; 403 K.

$$k_4/k_9(383 \text{ K}) = \frac{(d[H_2 \overrightarrow{\text{COCHCHO}}]/dt)_{\text{initial}}[1-C_4H_8]_{\text{initial}}}{(d[H_2 \overrightarrow{\text{COCHC}}_2H_5]/dt)_{\text{initial}}[C_2H_3 \overrightarrow{\text{CHO}}]_{\text{initial}}} = 1.33 \pm 0.31 \quad \text{(II)}$$

The rate constant for the epoxidation of 1-butene (9) has been determined ( $k_9 = 8.7 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1} \exp(-28.9 \text{ kJ mol}^{-1}/\text{RT})$  (±65% at 383 K), [10]). Hence, the rate constant for the formation of glycidal-dehyde can be determined as  $k_4$  (383 K) = (1.3 ± 0.9)  $\times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . The co-oxidation of acetaldehyde and acrolein cannot be used over a large enough temperature range for Arrhenius parameters to be determined for the reaction, as below ca. 370 K the autoxidation of acetaldehyde is too slow to be useful and above ca. 400 K the further reaction of glycidaldehyde (10) is too rapid in comparison with its rate of formation.

$$CH_{3}C(O)O_{2} \cdot + H_{2}\dot{C}O\dot{C}HCHO \longrightarrow CH_{3}C(O)O_{2}H + H_{2}\dot{C}O\dot{C}H\dot{C}O \quad (10)$$

For example, at 403 K (Fig. 5), the concentration of butene oxide increases as expected, but that of glycidaldehyde appears essentially constant. This behavior is consistent with the glycidaldehyde being both produced and consumed by peracetyl radicals (4 and 10) and from steady-state analysis:

$$k_4/k_{10} = [\text{H}_2\text{COCHCHO}]/[\text{C}_2\text{H}_3\text{CHO}]$$
  
= (6.2 ± 0.5) × 10<sup>-3</sup> (III)

The rate constant  $k_4$  measured at 383 K can be extrapolated to 403 K by assuming an A factor for the reaction of  $1.3 \times 10^8$  dm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup>, which is the average of epoxidation A factors that have been measured [14], giving  $k_{10}$  (403 K) =  $(3.3 \pm 2.3) \times 10^6$  dm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup>, which is three orders of magnitude faster than abstraction from acrolein. Since the yield of peracetic acid increases with time, while the yield of epoxide does not decrease with time, it is unlikely that consumption of the epoxide by reaction with the peracid is significant for this experiment.

Similarly, for the results described by Figure 4, epoxidation of acrolein and 1-butene by peracetic acid is unlikely to be significant, as the rates of formation of the two epoxides are essentially unvarying, while the concentration of the peracetic acid increases with time. This is consistent with previous studies which found that epoxidation by peracetic acid was always minor in comparison with epoxidation by acetylperoxyl radicals, in the early stages of the reaction [10,15,16].

It is known that rate constants for the epoxidation of alkenes by peroxyl radicals correlate well to the ionization energy of the double bond, with a lower ionization energy giving a faster reaction [15,17]. This is taken to indicate a degree of charge transfer at the transition state for the initial addition of the peroxyl radical to the double bond. The correlation for the addition of acetylperoxyl radicals to a series of substituted ethenes from propene to 2-methyl-2-butene [10,15,16] is given in Figure 6. Also included is the rate constant for the epoxidation of acrolein, which appears to be anomalously fast (by two orders of magnitude) in comparison with extrapolation of the behavior of the epoxidation of the alkenes. The second major photoionization peak at 1055 kJ mol<sup>-1</sup> has been used as a measure of the ionization energy of the C = C double bond, as the first photoionization peak at 975 kJ mol<sup>-1</sup> [18] is thought to be due to removal of an electron from an orbital situated mainly on the carbonyl oxygen atom [19]. The anomalously fast rate for the epoxidation of acrolein may provide an explanation for the autoxidation of acrolein at relatively low temperatures (ca. 513 K) being considerably slower than that of acetaldehyde or propanal [20]. Chain branching during aldehyde autoxidation is generally thought to be by decomposition of the acyl hydroperoxide: for example, for acetaldehyde,



**Figure 6** The correlation between the rate constant for epoxidation of alkenes by acetylperoxyl radicals (*k*) at 393 K [10,15,16] and the ionization energy [21] of the C==C double bond of alkenes (•), showing the anomalous behavior of acrolein (+) (at 383 K). The error limits represent the standard errors in the ratio of the epoxidation rate constant to that of the reference reaction with which they were all measured, the abstraction of the acyl hydrogen atom from acetaldehyde by acetylperoxyl radicals.

$$CH_{3}CHO + CH_{3}C(O)O_{2} \cdot \xrightarrow{} CH_{3}\dot{C}O + CH_{3}C(O)O_{2}H \quad (6)$$

$$CH_3C(O)O_2H \longrightarrow CH_3 \cdot + CO_2 + \cdot OH$$
 (11)

It is known that the addition of small quantities of alkene to reacting mixtures of acetaldehyde and oxygen can greatly inhibit the autoxidation of the aldehyde, due to an alternative reaction for the acylperoxyl radical, epoxidation of the alkene, competing with the formation of the peroxide (4) [10]. For example, for the addition of propene:

$$CH_3C(O)O_2 \cdot + C_3H_6 \xrightarrow{} CH_3 \cdot + CO_2 + C_3H_6O \quad (12)$$

The slow rate of acrolein autoxidation could be due to the relatively fast epoxidation of the carbon-carbon double bond by acrylperoxyl radicals (13), preventing the formation of the acrylhydroperoxide branching agent by the relatively slow abstraction of the acyl hydrogen by acrylhydroperoxyl radicals (14):

$$C_2H_3C(O)O_2 \cdot + C_2H_3CHO \longrightarrow C_2H_3 + CO_2 + H_2COCHCHO$$
 (13)

$$C_{2}H_{3}C(O)O_{2} \cdot + C_{2}H_{3}CHO \longrightarrow C_{2}H_{3}C(O)O_{2}H + C_{2}H_{3}CO \quad (14)$$

Likewise, the assumption that any acrolein formed during alkene autoxidation will react exclusively by abstraction of the acyl hydrogen is unlikely to be valid, with epoxidation by peroxyl radicals being a possible major alternative route. It is also evident that glycidaldehyde is much more reactive toward peroxyl radicals than the parent aldehyde, so it would be unlikely to build up to significant levels during alkene autoxidation. Indeed, in preliminary work on propene autoxidation, glycidaldehyde was only found in trace quantities [7].

### CONCLUSION

The epoxidation of acrolein by acetylperoxyl radicals has been examined and found to be anomalously fast, in comparison with the epoxidation of alkenes. The competing reaction of abstraction of the acyl hydrogen atom is considerably slower than from acetaldehyde or propanal. Both results suggest that acrolein formed during alkene autoxidation will be consumed by epoxidation, and not solely by abstraction of the acyl hydrogen as has been assumed previously. The epoxidation of the acrolein double bond also provides an explanation for the autoxidation of acrolein being considerably slower than that of acetaldehyde or propanal, through inhibiting the formation of the acylhydroperoxide branching agent by providing an alternative reaction for the peroxyl radicals.

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