

Epoxidation of Methacrolein by Acetylperoxyl Radicals

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An understanding of the mechanism of the gas phase autoxidation of alkenes depends in turn on an understanding of one the main primary products, the unsaturated aldehydes.¹ However, little work has been done on these species, though it is known that their low temperature autoxidation is anomalously slow in comparison with the oxidation of the equivalent saturated aldehyde.²

Recent work on the example of acrolein has established that this is because the acyl hydrogen atom is bonded unusually strongly, and also that peroxy radical addition to the C=C double bond is anomalously fast in comparison with unsubstituted alkenes,³ so that epoxidation of the aldehyde effectively competes with, and prevents, the formation of hydroperoxide branching agents.⁴

To further the investigation of the behaviour of conjugated unsaturated aldehydes, the rate of addition of acetylperoxyl radicals to methacrolein (reaction 1) has been examined by monitoring the formation of the resulting epoxide, over the temperature range 383 - 433 K and Arrhenius parameters have been determined. Acetylperoxy radicals were produced by co-oxidation of acetaldehyde with small quantities of methacrolein and a previously studied reference alkene, 2-methylpropene.⁵



$$\log_{10}(k_1/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) \approx 9.1 \pm 0.7 - (35.4 \pm 4.4) \text{ kJ mol}^{-1} / 2.203 \text{ RT}$$

The value of $\log_{10}(k_1/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = 4.41 \pm 0.08$ as determined at 393 K is compared in Figure 1 with rates for the addition of acetylperoxyl radicals to acrolein, as well as other unsubstituted alkenes. They are plotted against the ionisation energy of the C=C double bond, and it is apparent that the rate constants for the unsaturated aldehydes are *ca.* three orders of magnitude faster than would be expected if they conformed to the correlation between rate constant and ionisation energy that exists for the unsubstituted alkenes.³

Whilst the pre-exponential factor at $\log_{10}(A_1/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = 9.1 \pm 0.7$ is some ten

times greater than is typical for unsubstituted alkenes ($\log_{10}(A_{\text{alkene}}/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) \approx 8.1 \pm 0.5$), this cannot alone account for the fast rate of addition to conjugated unsaturated aldehydes. Therefore, the anomalously rapid rate of reaction for this class of compound must be predominantly due to a lowering of the barrier for the addition to the C=C bond by the adjacent carbonyl group.

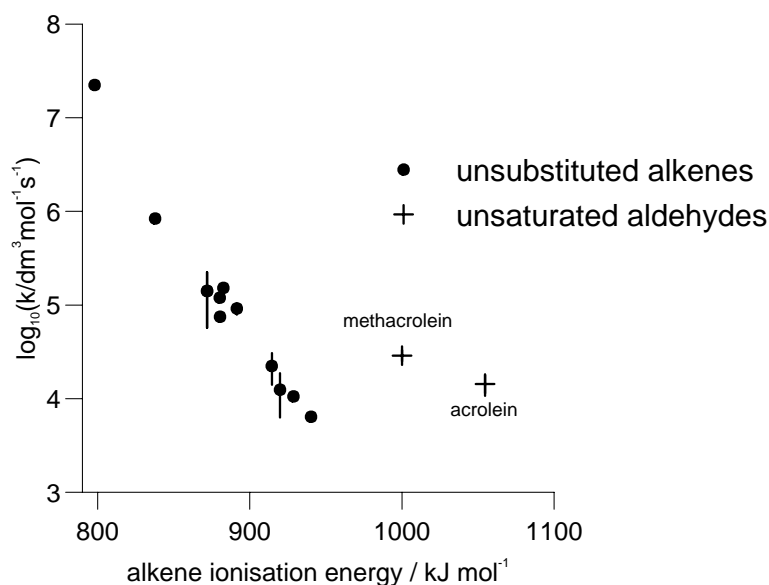


Figure 1: Correlation between alkene ionisation energies and the rate constants for the epoxidation of C=C double bonds by acetylperoxy radicals at 393 K,^{3,5} showing the anomalous behaviour of acrolein,⁴ and methacrolein (this work).

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