Experimental and Theoretical Study of the Atmospheric Degradation of Aldehydes

Barbara D'Anna and Claus J. Nielsen

Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo, Norway

Introduction

Aldehydes are ubiquitous key components in the chemistry of the troposphere. They are common primary pollutants from biogenic emissions and in residues of incomplete combustion (Ciccioli et al., 1993). Relevant natural sources are vegetation, forest fires and microbiological processes (Kotzias et al., 1997). Aldehydes are also nearly mandatory intermediates in the photo-oxidation processes of most organic compounds in the troposphere (Kerr and Sheppard, 1981; Carlier et al., 1986). Formaldehyde (HCHO) and acetaldehyde (CH₃CHO) are among the most abundant carbonyls in the atmosphere. Ambient levels are in the order of a few tens of pptv in clean background conditions (Zhou et al., 1996; Ayers et al., 1997) but may reach tens of ppbv in polluted urban areas as a consequence of the elevated anthropogenic emissions of aldehydes and their precursors from automobile traffic, industrial and domestic heating, and industrial activity (Carlier et al., 1986; Yokouchi et al., 1990). The atmospheric loss processes include photolysis, day-time reaction with OH radicals and with Cl and Br atoms in the marine boundary layer, and reaction with NO₃ radicals during the night-time. The photolytic cleavage of aldehydes constitute an important source of free radicals, particularly in the moderately and strongly polluted areas (Carlier et al., 1986; Yokouchi et al., 1990). Aldehydes are toxic compounds themselves, and some of their photo-oxidation products, the peroxyacylnitrates, are phytotoxic and strong eye-irritant compounds (Carlier et al., 1986; Carter et al., 1981). Further, peroxyacylnitrates, such as peroxyacetyl-nitrile (PAN), are long-lived species, which can act as a NO₂ reservoir in the troposphere.

Experimental studies

Two recent research projects, financed through the CEC Environment and Climate program, have addressed the atmospheric chemistry of aldehydes (RADICAL, 2000; CATOME, 2000), and a number of results from these studies have appeared in the literature (Beukes et al., 2000; Ullerstam et al., 2000; D'Anna et al., 2001a, 2001b, 2002). Other results have been published by the Atkinson group (Papagni et al., 2000).

For all the aliphatic aldehydes studied so far the Cl and Br reactions show small, positive activation energies (Atkinson et al., 1997), the OH reactions show negative activation energies (Atkinson, 1994), while the NO₃ reactions show activation energies of more than 10 kJ mol⁻¹ (Atkinson, 1994; Ullerstam et al., 2000; D'Anna et al., 2001a). The larger aliphatic aldehydes show reactivities

![Reaction rate coefficients](image)

*Figure 1.* Calculated vs. observed reaction rate coefficients at 298 K for the OH reaction with aliphatic aldehydes. The calculated reaction rate coefficients are based on the structure-reactivity by Kwok and Atkinson (1995).

towards OH and NO₃ radicals deviating from commonly used structure activity relations. This is illustrated in Figure 1 for the OH reactions. One may also note that the structure activity relationship for the NO₃ reactions with organics (Atkinson, 1991) fails completely for the aldehydes (D’Anna et al., 2001b).

In a so-called linear free energy plot showing log(κNO₃) vs. log(κOH), Figure 2, the reaction rate coefficients fall close to the correlation line for addition reactions in spite the fact that the reactions are abstraction reactions, see below (D’Anna and Nielsen, 1997; D’Anna et al., 2001b).

Aliphatic aldehydes may in principle react with radicals either by H-abstraction or by addition of the radical to the π-electron system. This is illustrated below using acetaldehyde as the example:

\[
\begin{align*}
X + \text{CH}_2\text{CHO} & \rightarrow \text{CH}_3\text{C}X\text{O} + \text{H} \quad (a) \\
& \rightarrow \text{CH}_3 + \text{XCHO} \quad (b) \\
& \rightarrow \text{CH}_3\text{CO} + \text{HX} \quad (c) \\
& \rightarrow \text{CH}_3 + \text{HX} + \text{CO} \quad (d) \\
& \rightarrow \text{CH}_2\text{CHO} + \text{HX} \quad (e)
\end{align*}
\]

Channels (a) and (b) may be termed as addition reactions, while the other three are H-abstraction reactions. According to thermodynamic data (Atkinson et al., 1997, and references therein) and to quantum chemical results (Beukes et al., 2000; D’Anna et al., 2002) all channels should be open to reaction for F and OH, channels (c)-(e) should be open to reaction for Cl and NO₃, while Br may only react through channel (c).

There are three product studies of the Cl reaction with acetaldehyde (Niki et al., 1985; Wallington et al., 1988; Beukes et al., 2000) and all conclude that less than 5% of the reaction proceeds through Hₐₙₐₐₜ abstraction. There are no similar studies of the Cl reaction with the larger aldehydes.

Results from studies of the regioselectivity of the NO₃ reaction with aldehydes have been presented (D’Anna et al., 2001a, 2001b). The results for acetaldehyde and butanal both imply that more than 95% of the NO₃ reaction proceeds through Hₐₚₜ abstraction. There are no systematic studies of the OH reaction paths for the larger aldehydes. However, results for acetaldehyde set upper limits of 2.5 and 2% through the addition channels (a) and (b), respectively, and 10% in total to channel (d) and to the Hₐₚₜ abstraction reaction (D’Anna et al., 2002).

Additional insight into the reaction mechanisms may be obtained from studies of the isotopic signature of reaction. Kinetic isotope effects have been reported for Cl reactions with formaldehyde and acetaldehyde (Niki et al., 1978; Beukes et al., 2000), and unusually large kinetic isotope effects are reported in the similar bromine reactions (Beukes et al., 2000). Isotopic data are available for the OH reactions with formaldehyde (Morris and Niki, 1971; Niki et al., 1984; D’Anna et al., 2002) and acetaldehyde (Taylor et al., 1996; D’Anna et al., 2002). Kinetic isotope effects have also been reported in the NO₃ radical reactions with formaldehyde and acetaldehyde (D’Anna et al., 2001; D’Anna et al., 2002). The experimental kinetic isotope effects observed in the formaldehyde reactions are summarised in Table 1.
Table 1. Experimental kinetic isotope effects for the reactions of Cl, Br, NO₃ and OH radicals with formaldehyde at 298 K.

<table>
<thead>
<tr>
<th>kₓ/kₓ</th>
<th>HCHO/DCDO</th>
<th>H¹³CHO/DCDO</th>
<th>HCHO/H¹³CHO</th>
<th>HCHO/DCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl 1.302 ± 0.014ₐ</td>
<td>1.217 ± 0.025ₐ</td>
<td>1.3 ± 0.2 b</td>
<td>6.8 ± 0.4ₐ</td>
<td></td>
</tr>
<tr>
<td>Br 7.5 ± 0.4ₐ</td>
<td>6.8 ± 0.4ₐ</td>
<td>2.97 ± 0.14 c</td>
<td>0.97 ± 0.02 c</td>
<td></td>
</tr>
<tr>
<td>NO₃ 1.62 ± 0.08 c</td>
<td>1.64 ± 0.12 c</td>
<td>0.97 ± 0.11 c</td>
<td>~1 d</td>
<td></td>
</tr>
<tr>
<td>OH 2.97 ± 0.14 c</td>
<td>0.97 ± 0.11 c</td>
<td>~1 d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


In summary, there is overwhelming experimental evidence of the Cl, Br, NO₃ and OH reactions with aliphatic aldehydes being primarily H₃₀H-abstraction reactions and not addition reactions. It is therefore somewhat puzzling why their reactivity towards OH and NO₃ radicals apparently fall on the addition line in a linear free energy plot, Fig. 2. It should also be noted that common to all the experimental isotopic signatures is the fact that it is neither possible to reproduce the trends nor the actual magnitudes satisfactory by conventional transition state theory (Beukes et al., 2000; D’Anna et al., 2002).

Theoretical studies

The reactions of F, Cl, Br, NO₃ and OH radicals with formaldehyde and acetaldehyde were recently studied by quantum chemical methods on the MP2 and CCSD(T) levels of theory (Beukes et al., 2000; D’Anna et al., 2002). The calculations indicate the existence of weak adducts in which the radicals in all cases are bonded to the aldehydeic oxygen. Transition states of the reactions X + HCHO → products, and X + CH₂CHO → products have been located, and energy level diagrams for reactants, intermediates and products in the reactions have been presented and discussed in relation to the observed product distributions. For the F, Cl, Br and NO₃ reactions the rate determining transition states are situated above the entrance channel. However, for the OH reactions the transition states to H₃₀H-abstraction are below the entrance channels. The relevant energy levels for formaldehyde/OH are illustrated in Figure 3.

![Figure 3](image-url)  
Figure 3. Energy levels, E_{CCSD(T)} + E_{ZPE}, of the OH + HCHO reaction system calculated at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level.
As can be seen from Figure 3 the barrier to $H_{\text{ald}}$-abstraction is calculated to be negative relative to the reactants energy, $E_{\text{CCSD(T)}} + E_{\text{ZPE}} = -5.8 \text{ kJ mol}^{-1}$ (D'Anna et al., 2002), and that the OH radicals form both pre- and post-reaction adducts with the substrate. The energy of the pre-reaction adduct, including the zero point energy, is ca. $-11 \text{ kJ mol}^{-1}$ relative to that of the reactants. As to the relative importance of two channels in the $H_{\text{ald}}$-abstraction reaction, channel (c) conform with the minimum energy path leading from the transition state via an adduct to the products, $\text{HCO} + \text{H}_2\text{O}$, without any barrier, whereas channel (d) involves a barrier of ca. $70 \text{ kJ mol}^{-1}$ to the elimination of the hydrogen atom.

Figure 4 shows the OH–HCHO structures of the pre- and post-reaction adducts together with that of the transition state to $H_{\text{ald}}$-abstraction. The figure also includes the more interesting bond distances and the imaginary frequency corresponding to the negative eigenvalue of the Hessian matrix.

The barrier to OH addition to the carbonyl carbon was calculated as ca. $28 \text{ kJ mol}^{-1}$ (D'Anna et al., 2002) and the structure of the transition state is included in Figure 4. Previous studies report barriers ranging from 34 to $43 \text{ kJ mol}^{-1}$ depending on the method of calculation (Soto and Page, 1990; Alvarez-IIdaoy et al., 2001). In any case, the barrier to the OH addition reaction with formaldehyde is so high that pathway (a) to the formation of HCOOH has little importance under atmospheric conditions.

![Figure 4](attachment:figure4.png)

**Figure 4.** MP2/aug-cc-pVDZ structures of stationary points in the OH + HCHO $\rightarrow$ HCO + H$_2$O reaction: (A) the pre-reaction adduct, (B) the transition state, (C) the post-reaction adduct; (D) the transition state of the OH addition reaction, OH + HCHO $\rightarrow$ HCOOH + H$_2$O. Distances in Å, values in parenthesis refer to the free molecule.

Very similar results are obtained for the acetaldehyde–OH system (D'Anna et al., 2002). In the $H_{\text{ald}}$-abstraction pathway the OH radicals form pre- and post-reaction adducts with the substrate. The barrier to $H_{\text{ald}}$-abstraction is below the entrance channel, ca. $-14 \text{ kJ mol}^{-1}$. The minimum energy path from the transition state to $H_{\text{ald}}$-abstraction is via a water adduct to the reactants, CH$_3$CO + H$_2$O, without any barrier. The alternative channel (d) involves a barrier of ca. $70 \text{ kJ mol}^{-1}$ to the formation of CH$_3$ + CO + H$_2$O. Although the transition state towards C-C bond breakage in channel (d) is ca. $50 \text{ kJ mol}^{-1}$ below the energy of the reactants, it is more likely that the excess energy of reaction is channeled into the loose bond to water than into C-C bond breakage. That is, from the theoretical results alone channel (c) is expected to dominate the reaction. The minimum energy path to $H_{\text{methyl}}$-abstraction is also via pre- and post-reaction adducts and the barrier to $H_{\text{methyl}}$-abstraction is calculated as only $12 \text{ kJ mol}^{-1}$. In any case, the barrier to $H_{\text{methyl}}$-abstraction is so high that channel (c) is of little importance at atmospheric conditions. The barrier to OH addition to the carbonyl carbon, the first step of channels (a) and (b), is calculated as ca. $31 \text{ kJ mol}^{-1}$. The addition channel is therefore of no importance under atmospheric conditions.

In summary, the theoretical calculations indicate that $H_{\text{ald}}$-abstraction is by far the dominating reaction of OH with acetaldehyde. In all likelihood, the same is true for the larger aldehydes as well.

Rates of the OH reactions with formaldehyde and acetaldehyde have been derived from general expressions based on RRKM theory (D'Anna et al., 2002) following the method by
Jodkowski et al. (1998). In the case of acetaldehyde, the OH radical forms two H-bonded adducts, one with the oxygen oriented towards $H_{\text{ald}}$ ($A_{\text{ald}}$), and one with oxygen oriented towards $H_{\text{meth}}$ ($A_{\text{meth}}$), separated by a very low energy barrier ($TS_{\text{ald-meth}}$). The following model was assumed:

$$\text{OH} + \text{CH}_2\text{CHO} \leftrightarrow A_{\text{meth}} \leftrightarrow TS_{\text{ald-meth}} \leftrightarrow A_{\text{ald}} \leftrightarrow TS_{\text{Hald-abstraction}} \leftrightarrow \text{Products}$$

Taking the structures and energies obtained by the quantum chemical calculations it was not only possible to reproduce the overall temperature dependence of the reactions, but also to calculate the kinetic isotopic signatures (D'Anna et al., 2002). Figure 5 shows a comparison between the experimental data and the calculated reaction rate coefficient.

![Graph showing rate coefficients](image)

**Figure 5.** Observed and calculated rate coefficients of the reaction $\text{OH} + \text{CH}_2\text{CHO} \rightarrow \text{products}$. Data taken from Atkinson (1994) (●) and from Taylor et al. (1996) (○). Dotted curve: Rate coefficient for direct $H_{\text{ald}}$-abstraction. Dashed curve: Rate coefficient for (indirect) $H_{\text{ald}}$-abstraction via initial adduct formation. Full curve: Sum of the rate coefficients for direct and indirect $H_{\text{ald}}$-abstraction.

**Acknowledgement**

This work is part of the project “Carbonyls in Tropospheric Oxidation Mechanisms” (CATOME) and has received support from the CEC Environment and Climate program through contract ENV4-CT97-0416.

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