Central role of carbonyl compounds in atmospheric chemistry

D. J. Lary[1]

Department of Geophysics and Planetary Sciences, Tel Aviv University, Tel Aviv, Israel

D. E. Shallcross[2]

Centre for Atmospheric Science, Cambridge University, Cambridge, England, United Kingdom

Abstract. With the exception of acetone it is not generally recognized how important atmospheric carbonyls and alkyl radicals are in the lower stratosphere and upper troposphere. Carbonyl compounds are the crucial intermediate species for the autocatalytic production of OH. For example, in the upper troposphere and lower stratosphere it is calculated based on data assimilation analysis of Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) data that CH_3 production due to the degradation of carbonyls contributes around 40% to the overall production of CH_3, a key initiation step for HO_x production, with the contribution due to the photolysis of CH_3CHO being comparable to that of acetone. So correctly modeling the alkyl radical concentrations is of central importance and has not be given the attention it deserves to date. The reactions of carbonyls with Br and Cl are also major sources of HBr and HCl. In short, carbonyl compounds play a central role in atmospheric chemistry close to the tropopause, and this is directly relevant to issues such as the assessment of the impact of air traffic, and ozone depletion.

1. Introduction

The recent World Meteorological Organization [1998] (WMO) report report concludes that our understanding of tropospheric OH is incomplete, especially with regard to sources of upper tropospheric OH and the chemistry of polluted conditions. This is particularly significant when we recall that HO_x cycles are the dominant catalytic ozone loss cycles in midlatitudes below 20 km [Lary, 1997; WMO, 1998].

Aldehydes and ketones are key intermediates in atmospheric chemistry. In the atmosphere they are produced by the oxidation of hydrocarbons, and some are also emitted directly (e.g., acetone). Because they undergo a wide variety of reactions, both chemical and photolytic, they play a major role in many atmospheric processes. Notably, the >C=O group is a chromophore allowing absorption to occur at long wavelengths. The reactivity of these compounds arises largely through two features of their structures: the polarity of the carbonyl group and the acidity of any alpha hydrogens that are present.

The sections which follow review the major roles of atmospheric carbonyls. However, before examining the atmospheric chemistry of carbonyls in more detail, let us examine the credentials of the photochemical model.

2. Model Calculation

The numerical model used in this study is the extensively validated AutoChem model [Lary et al., 1995b; Lary, 1996; Fisher and Lary, 1995; Wang et al., 2000]. The model is explicit and uses the adaptive-timestep, error monitoring, [Stoer and Bulirsch, 1980] time integration scheme designed by Press et al. [1992] for stiff systems of equations.

Photolysis rates are calculated using full spherical geometry and multiple scattering as described by Lary and Pyle [1991a, b] after Meier et al. [1982]; Nicolet et al. [1982] with the treatment of spherical geometry after Anderson [1983]. The photolysis rate used for each time step is obtained by 10 point Gaussian-Legendre integration after Press et al. [1992]. The time step usually used is 15 min.

AutoChem uses kinetic data largely based on DeMore et al. [1997] and Atkinson et al. [1997], with the recent NO_2 and HNO_3 kinetics of Donahue et al. [1997], Fulle et al. [1998], Brown et al. [1999a], and Portmann et al. [1999] evaluated by Brown et al. [1999b], and the recent OH+ClO kinetics of Kegley Owen et al. [1999].

---

[1] Also at the Centre for Atmospheric Science, Cambridge University, Cambridge, England, United Kingdom.

[2] Now at the School of Chemistry, University of Bristol, Bristol, England, United Kingdom.

In addition, it was the first model to ever have the facility to perform 4D variational data assimilation (4D-VAR) [Fisher and Lary, 1995]. This is a "state of the art" technique used extensively in meteorology. The use of data assimilation in atmospheric chemistry has been reviewed by Lary [1999]. It allows us to bring together within a mathematical framework our observational and theoretical knowledge together with their associated uncertainties. In a least squares sense it provides the best fit simulation of the model to any available observations within the assimilation period. In this case it was a 1-day period of data from the space shuttle borne Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) instrument [Abrams et al., 1996; Newchurch et al., 1996]. Observations of 16 species measured by ATMOS and the Upper Atmosphere Research Satellite (UARS) were simultaneously used, namely: O_3, NO, NO_2, N_2O_5, HNO_3, HO_2NO_2, HCN, ClO, $ClONO_2$, N_2O, CO, CO_2, CH_4, C_2H_6, and H_2O, together with Stratospheric Aerosol and Gas Experiment (SAGE) aerosol observations. The model is therefore highly constrained, and so any deficiency in our kinetic description is readily highlighted. As this "state of the art" technique is not yet widely used in atmospheric chemistry it is valuable to mention the works by Menke [1984], Courtier and Talagrand [1987], Cohn [1997], Courtier et al. [1993], Fisher and Lary [1995], Khattatov et al. [1999], and Lary [1999].

In this study no description of atmospheric transport or convection has been used. Instead the 4D-VAR data assimilation was performed using a set of stacked, independent, boxes. The boxes were stacked in the equivalent-PV latitude theta flow tracking coordinate system [Lary et al., 1995a] at an equivalent PV latitude of 40°S. 40°S was chosen as we used data from the STS-45/ATLAS 1 mission which was launched on March 24, 1993 from the Kennedy Space Center. During its 8 days of operation, the ATMOS instrument made observations spanning a substantial portion of the globe. The 53 measurements taken at orbital sunrise covered the midlatitude and equatorial regions of the Earth from 30°S to 30°N. The 41 sunset observations were made at 25°S to 55°S. For the duration of ATLAS-1 the equivalent PV latitude for which the vertical profiles covered the largest range of altitudes, and for which the largest number of species were observed, was centered on about 40°S. The assimilation window used was 1-day so that we can have one complete diurnal cycle.

2.1 Validation

Since the concentrations of the hydrocarbons used is such a crucial factor in the reliability of the analysis presented here, Figure 1 shows a comparison of the analyses produced with data assimilation for C_2H_6 and CH_4 and the ATMOS observations. We can see that in both cases the model falls well within the observed error bars. Space does not here permit to give further
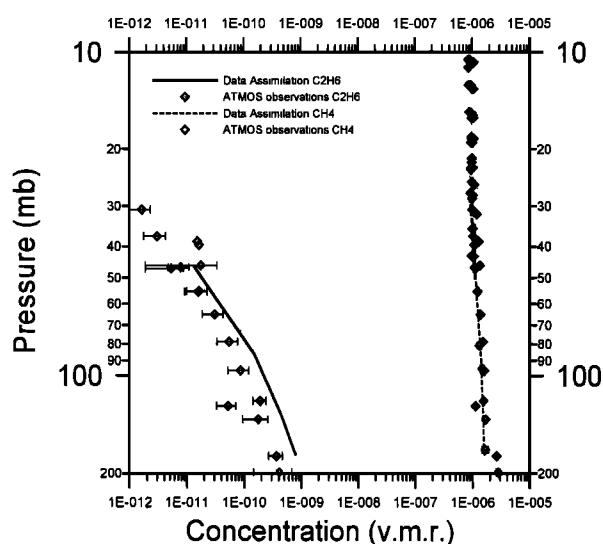

Figure 1. A comparison of the observed C_2H_6 and CH_4 concentrations obtained using data assimilation with the AutoChem model and the observations of ATMOS for 40°S at 17.45 local solar time on March 29, 1993. Observations of 15 species measured by ATMOS and UARS were simultaneously used, namely: O_3, NO, NO_2, N_2O_5, HNO_3, HO_2NO_2, HCN, ClO, $ClONO_2$, N_2O, CO, CO_2, CH_4, C_2H_6, and H_2O.

validation of the model. However, Lary and Shallcross [in press, 2000] showed comparison with the observed $ClONO_2$/HCl and NO_x/HNO_3 ratios and HBr obtained using data assimilation with the AutoChem model and the observations of ATMOS and other instruments and showed that in both cases the model falls well within the observed error bars. Likewise, later on in this paper a detailed comparison is given with insitu aircraft data from the Stratospheric Photochemistry Aerosol and Dynamics Experiment (SPADE).

2.2 Choice of Observations

Care needs to be taken when performing model data comparisons that like is compared with like. So in this study very careful data selection was performed to ensure that it really is suitable to use the observations we have used in our analysis. For example, atmospheric propane and acetone have been measured and would have been useful, but as we use very strict selection criteria in a flow tracking coordinate system (equivalent PV latitude and theta) and local solar time, unfortunately none were available for our analysis period. The two data sets we have used (ATMOS and SPADE) include simultaneous observations of many species. To the best of our knowledge, there are no simultaneous measurements of NMHC or carbonyls; that is the only reason that they were not used. We would, of course, rather that such observations were available to us, as then we could better constrain the calculations. We have used such rigorous selection criteria as it is vital

for us to compare like with like, otherwise the comparison is rather worthless.

2.3 A Unique Feature of Data Assimilation

It is worth noting something about the technique of data assimilation. It gives us indirect information on all the species within the chemical scheme via our theoretical model. This is a unique and powerful feature of this type of analysis. It is not just a simple model observation comparison, it is an optimized fit of the model to all of the observations. This unobserved specie information may of course may be incomplete if our model is incomplete, but as we can see from the SPADE study the shapes of diurnal cycles and the partitioning of species contains information on other, nonobserved, species.

3. Hydrocarbon Oxidation and the Possibility of Autocatalysis

The Earth's atmosphere is strongly oxidizing, and so hydrocarbons released into the atmosphere are oxidized. This eventually leads to the production of CO_2. Figure 2 shows schematically the oxidation of methane, ethane, and propane.

The oxidation is usually initiated by the abstraction of a hydrogen atom from the hydrocarbon by reaction with OH, $O(^1D)$, or Cl. Although for much of the troposphere the abstraction by OH is the most important, in the upper troposphere and lower stratosphere the abstraction by Cl becomes significant, even dominant. In regions where we have had chlorine activation on cold surfaces, then abstraction by Cl also dominates.

The alkyl radicals (CH_3, C_2H_5, or C_3H_7 generically refereed to as R) formed by hydrogen abstraction will immediately add to O_2 to form a peroxy radical (RO_2). Peroxy radicals formed in the lower stratosphere or upper troposphere will react with NO, ClO, or BrO, thereby coupling RO_x with NO_x ClO_x, and BrO_x, to yield an alkoxy radical RO. Including these RO_2 reactions can significantly alter the OH/HO_2, NO/NO_2, Cl/ClO, and Br/BrO ratios. For the alkoxy radicals investigated here, reaction with O_2 will dominate. For CH_3O, C_2H_5O and n-C_3H_7O, HO_2 and RCHO will be formed. Where RO is i-C_3H_7O acetone and HO_2 will be formed. The aldehydes will be photolyzed. Primarily producing HCO radicals, which on reaction with O_2 generate CO and HO_2, and another alkyl radical, which can feed back into the cycle depicted in Figure 2, giving more OH.

3.1 Importance of Alkyl, R, Radicals

It should be emphasised that the alkyl radicals, R, are the first step in hydrocarbon oxidation once a hydrogen has been abstracted from the alkanes. So their formation represents one of the key initiation steps of HO_x
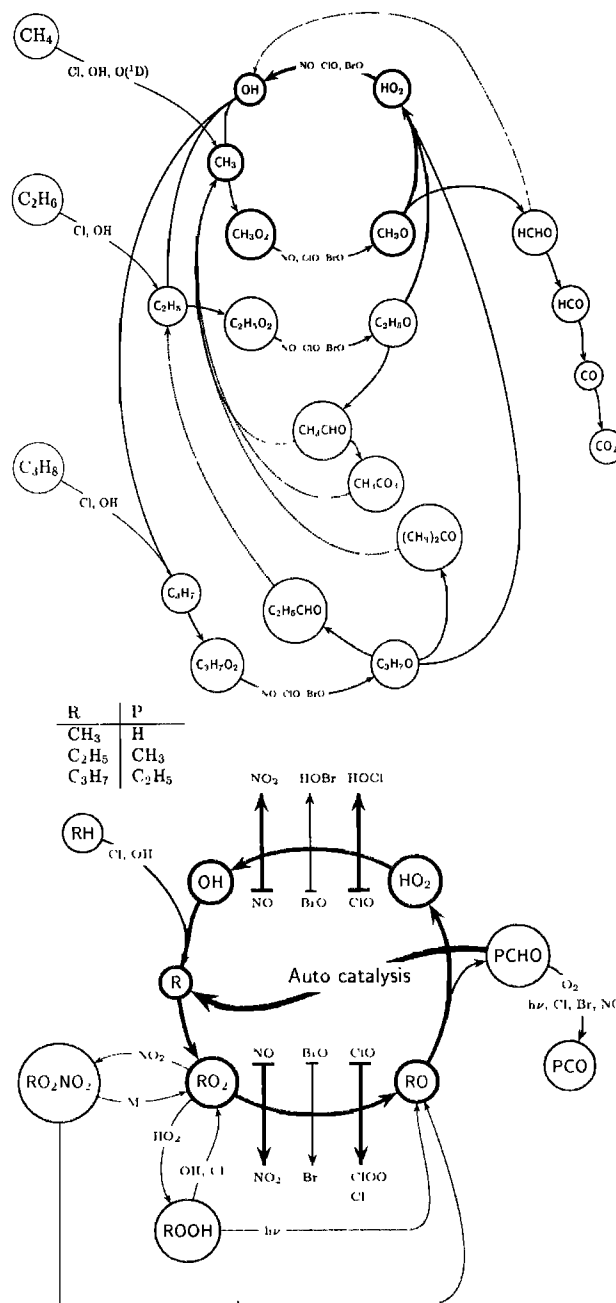

Figure 2. A schematic representation of methane, ethane, and propane oxidation.

production. As the diagram in Figure 2 shows, they are also the radicals formed in the autocatalysis where the carbonyls are fragmented, another key issue for HO_x production. This autocatalysis becomes a more significant source of CH_3 as you go down the series of alkanes from C2 to C3, etc. So correctly modeling the alkyl radical concentrations is one of central importance, and has not be given the attention it deserves to date.

3.2 Source of R Radicals and Hence OH

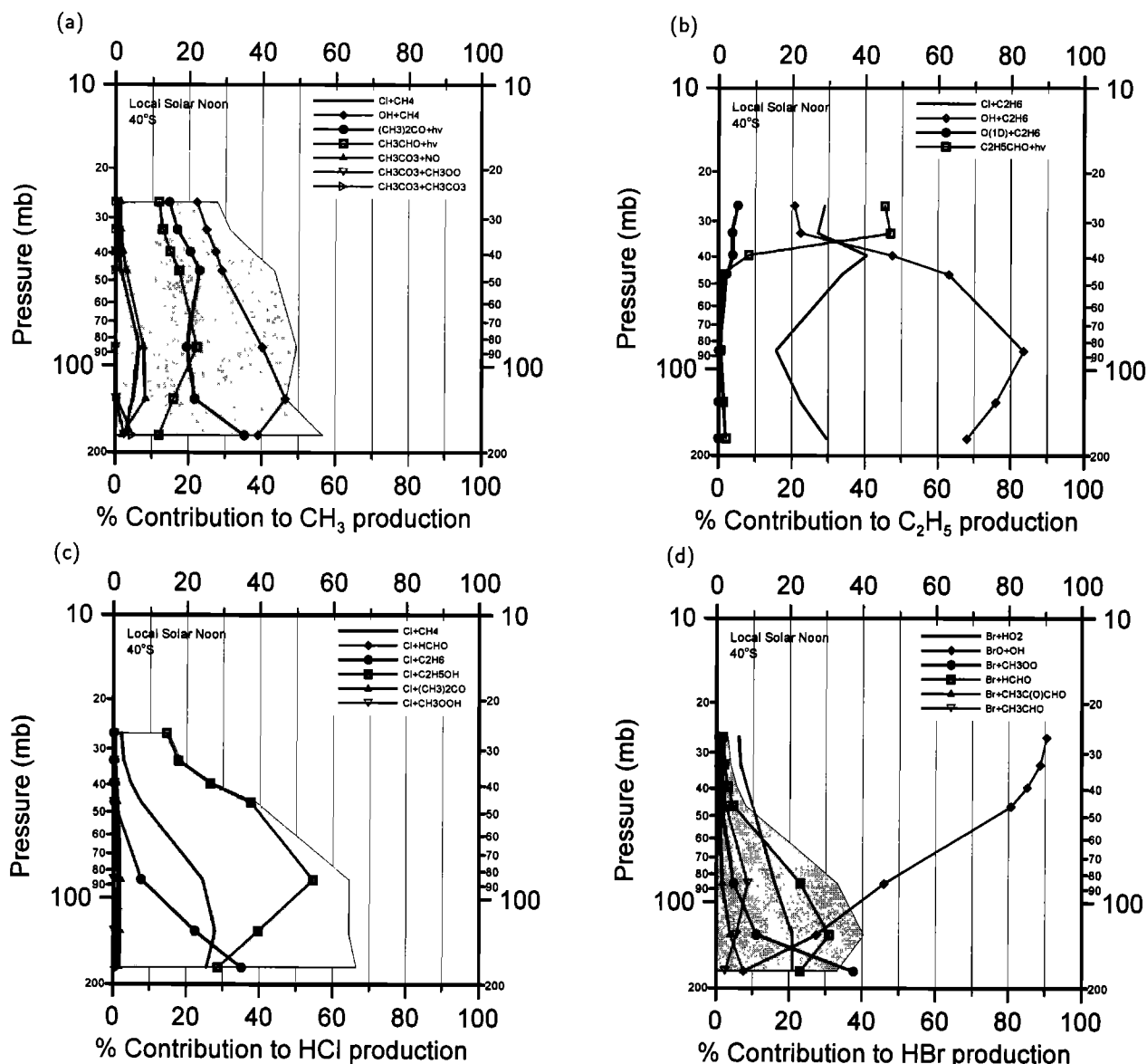What is seldom highlighted is the fact that in the upper troposphere and lower stratosphere the source of

(a)

Local Solar Noon
40°S

Pressure (mb)

Cl+CH4
OH+CH4
(CH3)2CO+hv
CH3CHO+hv
CH3CO3+NO
CH3CO3+CH3OO
CH3CO3+CH3CO3

% Contribution to CH_3 production

(b)

Local Solar Noon
40°S

Pressure (mb)

Cl+C2H6
OH+C2H6
O(1D)+C2H6
C2H5CHO+hv

% Contribution to C_2H_5 production

(c)

Local Solar Noon
40°S

Pressure (mb)

Cl+CH4
Cl+HCHO
Cl+C2H6
Cl+C2H5OH
Cl+(CH3)2CO
Cl+CH3OOH

% Contribution to HCl production

(d)

Local Solar Noon
40°S

Pressure (mb)

Br+HO2
BrO+OH
Br+CH3OO
Br+HCHO
Br+CH3C(O)CHO
Br+CH3CHO

% Contribution to HBr production

Figure 3. The calculated percentage contribution for local solar noon on March 29, 1993, at 40°S of the various reactions which produce (a) CH_3 (the background shading shows the total contribution to CH_3 production from carbonyls), (b) C_2H_5, (c) HCl (the background shading shows the contribution to HCl production from organic species not in most stratospheric models), and (d) HBr (the background shading shows the total contribution to HBr production from carbonyls). Obtained using data assimilation with the AutoChem model of observations of 15 species measured by ATMOS and UARS, namely: O_3, NO, NO_2, N_2O_5, HNO_3, HO_2NO_2, HCN, ClO, $ClONO_2$, N_2O, CO, CO_2, CH_4, C_2H_6, and H_2O.

our R radicals (i.e. CH_3, C_2H_5 etc.) from the decomposition of the carbonyls is often of comparable magnitude, and sometimes greater than that due to the initial hydrocarbon hydrogen abstraction by OH, $O(^1D)$, or Cl (Figure 3). For example, we have at least three sources of CH_3 from carbonyl compounds, acetone $((CH_3)_2CO)$ photolysis [*Gierczak et al.*, 1998; *McKeen et al.*, 1997; *Jaeglé et al.*, 1998], ethanal (CH_3CHO) photolysis [*Friedl et al.*, 1997], and the reaction of NO with CH_3CO_3. Consequently, we have an effective autocatalytic production of OH with the carbonyl compounds being the crucial intermediate species, and with auto-

catalysis being the catalysis of a reaction by one of its products.

Figure 3 shows the calculated percentage contribution for local solar noon on March 29, 1992, at 40°S of the reactions which produce CH_3 (Figure 3a) and C_2H_5 (Figure 3b). Figure 3a shows that in the upper troposphere and lower stratosphere one of most important sources of CH_3 is the photolysis of CH_3CHO which is comparable to that due to the photolysis of acetone.

Acetone is a major source of HO_x. For example, *Muller and Brasseur* [1999] recently reported model calculations that suggest that acetone photooxidation rep-

resents a large, almost ubiquitous source of HO_x in the upper troposphere (around 20-40% of the total primary source in the main aircraft corridors, poleward of 40°N), while the convective injections of peroxides and aldehydes are the dominant sources in the tropics, above the oceans and the continents, respectively. *Muller and Brasseur* [1999] calculated that the presence of acetone might enhance by about 20% the sensitivity of upper tropospheric ozone to the current aircraft emissions of NO_x.

In the case of C_2H_5, Figure 3b shows that hydrogen abstraction by Cl is an important source of C_2H_5. This again emphasizes the importance of hydrogen abstraction by halogens.

Figure 4 shows the effect of a comparison between observations and calculations obtained when the carbonyl sources of HO_x are included using the technique of 4D-Var data assimilation. Data assimilation allows us to simultaneously use all the observations together with our numerical model, to give us the best fit model simulation to the observations in a least squares sense. In some cases there is an improvement when the carbonyl sources of HO_x are included (namely, ClO and HCl), and in others there is a slight worsening of the fit (morning OH). The comparison is not conclusive.

The various curves correspond to progressively more complete chemical schemes. The solid line is a full methane oxidation scheme with 59 species and 366 reactions, the dashed curve is for a full methane-ethane oxidation scheme with 74 species and 431 reactions, the dot-dashed curve is for a full methane-ethane-propane oxidation scheme with 89 species and 492 reactions, the dot-dot-dashed curve is for a full methane-ethane-propane-ethene oxidation scheme with 107 species and 566 reactions. The overlying diamonds with error bars are the SPADE observations.

So two points are worth emphasizing. First, in the upper troposphere and lower stratosphere the reaction of Cl with C_2H_6 is much more important than the reaction of OH with C_2H_6. Second, the reaction of Cl with C_2H_6 producing the reservoir HCl offsets the reaction of Cl with O_3. So we have additional pathways for reducing the effectiveness of catalytic ozone loss by chlorine.

3.3 Interaction With Organic Aerosols

D. J. Lary et al. (The potential role of carbonyl production on organic aerosols, submitted to *Journal of Geophysical Research*, 1999) consider the possibility of atmospheric organic aerosols interacting with O_3 leading to the formation of aldehydes such as HCHO and CH_3CHO. They conclude that if organic aerosols do release carbonyls on reaction with O_3, then one of the most significant effects is likely to be the formation of hydrogen halides. It is likely that this will play a role if the product of the reaction probability and the organic surface area exceeds $2x10^{-4}$ μm^2 cm^{-3}. If the reac-

tion probabilities of [*deGouw and Lovejoy*, 1998] apply to these processes, then this corresponds to an organic aerosol surface area in the range 0.2 to 2 μm^2 cm^{-3}. The measurements of *Novakov and Penner* [1993] imply an organic surface area of the order of 3 μm^2 cm^{-3}; it is therefore possible that there is a role for these processes in the atmosphere. The next most significant effect is the autocatalytic production of OH which in turn will reduce the HNO_3/NO_y ratio. It is likely that this will play a role if the product of the reaction probability and the organic surface area exceeds $9x10^{-4}$ μm^2 cm^{-3}. *Fruekilde et al.* [1998] have also observed the formation of carbonyls from the ozonolysis of a leaf surface.

Recently *Murphy et al.* [1998] have reported that a very high fraction of tropospheric aerosols contain organic molecules; some presumably reside on the surface of the aerosols. *Murphy et al.* [1998] made in situ measurements of the chemical composition of individual aerosol particles at altitudes between 5 and 19 km. The measurements reveal that upper tropospheric aerosols often contained more organic material than sulfate. *Novakov and Penner* [1993], *Sheridan et al.* [1994], and *Novakov et al.* [1997] collected atmospheric particles in the mid-latitude upper troposphere and lower stratosphere, and they found non sulfate materials including carbon rich substances. Other measurements of organic aerosols have also been made, [e.g., *Middlebrook et al.*, 1998; *Shevchenko et al.*, 1999; *Kavouras et al.*, 1998; *Vasconcellos et al.*, 1998; *Chen et al.*, 1997].

4. The Production of Hydrogen Halides

Several observational and modeling studies have also highlighted the inability of the models to reproduce the observed HBr profile. These include the work of *Nolt et al.* [1997], *Chipperfield et al.* [1997], *Johnson et al.* [1995], and *Carlotti et al.* [1995]. The recent WMO [1998] report concludes that 30 km models usually overpredict the ClO/HCl and HOCl/HCl ratios.

Figure 3c shows that in the troposphere it is calculated that the main source of HCl is hydrogen abstraction by Cl from C_2H_6, CH_4, and C_2H_5OH. As we approach the tropopause and then enter the lower stratosphere, it is calculated that the reaction of Cl with C_2H_5OH becomes the most important. The role of carbonyl compounds is also important in the case of HBr (Figure 3d).

5. Summary

Carbonyl compounds are crucial intermediate species for the autocatalytic production of OH. It is calculated that at around 20 km the CH_3 production due to the degradation of carbonyls is almost twice as much as that due to the total direct H abstraction by OH, O(^{1}D), and Cl. This is particularly significant when we recall that
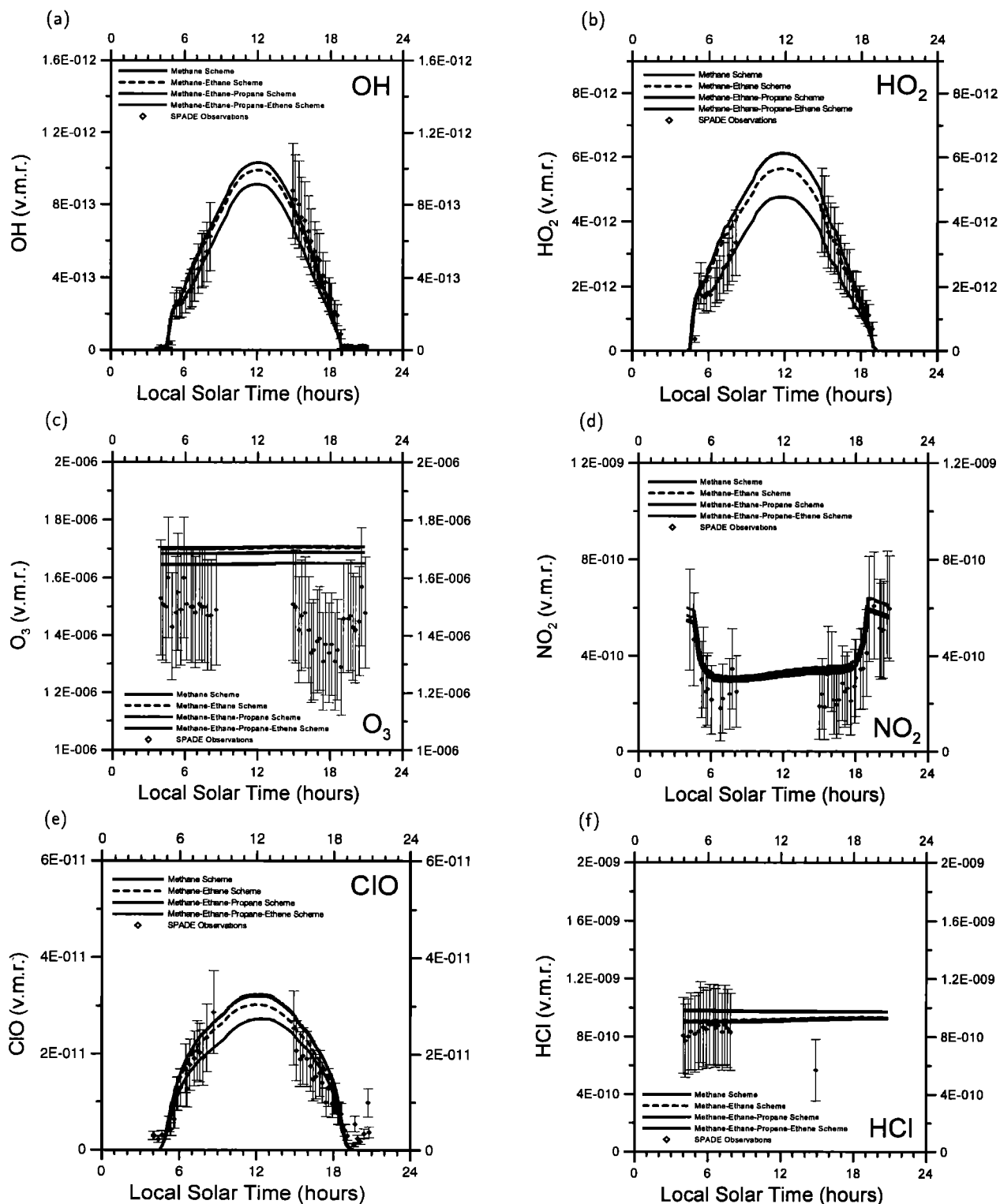
Figure 4. 4D-Var analysis of SPADE data taken from the ER-2. The various curves correspond to progressively more complete chemical schemes. The solid line is a full methane oxidation scheme with 59 species and 366 reactions, the dashed curve is for a full methane-ethane oxidation scheme with 74 species and 431 reactions, the dot-dashed curve is for a full methane-ethane-propane oxidation scheme with 89 species and 492 reactions, and the dot-dot-dashed curve is for a full methane-ethane-propane-ethene oxidation scheme with 107 species and 566 reactions. The overlying diamonds with error bars are the SPADE observations. (a) OH, (b) HO$_2$, (c) O$_3$, (d) NO$_2$, (e) ClO, and (f) HCl.

HO_x cycles are the dominant catalytic ozone loss cycles in midlatitudes below 20 km [*Lary*, 1997; *WMO*, 1998]. In addition, at around 10 km the photolysis of C_2H_5CHO contributes approximately 35% to the production of C_2H_5. Both CH_3 and C_2H_5 are at the start of the CH_4 and C_2H_6 oxidation chains.

The reaction of Br with carbonyls is the dominant source of HBr in the troposphere and lower stratosphere. It is therefore not surprising that many models have not been able to reproduce the observed HBr profile as these halogen carbonyl interactions are often not included in the model calculations [*Nolt et al.*, 1997; *Chipperfield et al.*, 1997; *Johnson et al.*, 1995; *Carlotti et al.*, 1995]. In short, carbonyl compounds play a central role in atmospheric chemistry.

References

Abrams, M., M. Gunson, A. Chang, C. Rinsland, and R. Zander, Remote sensing of the earth's atmosphere from space with highresolution Fourier-transform spectroscopy: Development and methodology of data processing for the ATMOS experiment, *Appl. Opt.*, *35*, 2774–2786, 1996.

Anderson, D., The troposphere-stratosphere radiation-field at twilight - A spherical model, *Planet. Space Sci.*, *31*, 1517–1523, 1983.

Atkinson, R., D. Baulch, R. Cox, R. Hampson, J. Kerr, M. Rossi, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VI., IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, *26*, 1329–1499, 1997.

Brown, S., R. Talukdar, and A. Ravishankara, Rate constants for the reaction $OH+NO_2 \longrightarrow HNO_3+M$ under atmospheric conditions, *Chem. Phys. Lett.*, *299*, 277–284, 1999a.

Brown, S., R. Talukdar, and A. Ravishankara, Reconsideration of the rate constant of the reaction of hydroxyl radicals with nitric acid, *J. Phys. Chem.*, *103*, 3031–3037, 1999b.

Carlotti, M., et al., Measurement of stratospheric HBr using high-resolution far-infrared spectroscopy, *Geophys. Res. Lett.*, *22*, 3207–3210, 1995.

Chen, S., S. Liao, W. Jian, and C. Lin, Particle size distribution of aerosol carbons in ambient air, *Environ. Int.*, *23*, 475–488, 1997.

Chipperfield, M., D. Shallcross, and D. Lary, A model study of the potential role of the reaction BrO+OH in the production of stratospheric HBr, *Geophys. Res. Lett.*, *24*, 3025–3028, 1997.

Cohn, S., An introduction to estimation theory, *J. Met. Soc. Japan*, *75*, 257–288, 1997.

Courtier, P., and O. Talagrand, Variational assimilation of meteorological observations with the adjoint vorticity equation., 2. Numerical results, *Q. J. R. Meteorol. Soc.*, *113*, 1329–1347, 1987.

Courtier, P., J. Derber, R. Errico, J. Louis, and T. Vukicevic, Important literature on the use of adjoint, variational-

methods and the Kalman filter in meteorology, *Tellus, Ser. A.*, *45A*, 342–357, 1993.

deGouw, J., and E. Lovejoy, Reactive uptake of ozone by liquid organic compounds, *Geophys. Res. Lett.*, *25*, 931–934, 1998.

DeMore, W. B., C. J. Howard, S. P. Sander, A. R. Ravishankara, D. M. Golden, C. E. Kolb, M. J. Hampson, R. F. Molina, and M. J. Kurylo, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 97-4 12*, 1997.

Donahue, N., M. Dubey, R. Mohrschladt, K. Demerjian, and J. Anderson, High-pressure flow study of the reactions $OH+NO_x= HNO_3$: Errors in the falloff region, *J. Geophys. Res.*, *102*, 6159–6168, 1997.

Fisher, M., and D. Lary, Lagrangian 4-dimensional variational data assimilation of chemical-species, *Q. J. R. Meteorol. Soc.*, *121*, 1681–1704, 1995.

Friedl, A., et al., Photochemistry of formaldehyde during the 1993 Tropospheric OH Potochemistry Experiment, *J. Geophys. Res.*, *102*, 6283–6296, 1997.

Fruekilde, P., J. Hjorth, N. Jensen, D. Kotzias, and B. Larsen, Ozonolysis at vegetation surfaces: A source of acetone, 4-oxopentanal, 6-methyl-5-hepten-2-one, and geranyl acetone in the troposphere, *Atmos. Environ.*, *32*, 1893–1902, 1998.

Fulle, D., H. Hamann, H. Hippler, and J. Troe, Temperature and pressure dependence of the addition reactions of OH to NO and to NO_2., IV. Saturated laser-induced fluorescence measurements up to 1400 bar, *J. Phys. Chem. Ref. Data*, *108*, 5391–5397, 1998.

Gierczak, T., J. Burkholder, S. Bauerle, and A. Ravishankara, Photochemistry of acetone under tropospheric conditions, *Chem. Phys.*, *231*, 229–244, 1998.

Jaeglé, L., D. Jacob, Y. Wang, A. Weinheimer, B. Ridley, T. Campos, G. Sachse, and D. Hagen, Sources and chemistry of NO_x in the upper troposphere over the United States, *Geophys. Res. Lett.*, *25*, 1705–1708, 1998.

Johnson, D., W. Traub, K. Chance, and K. Jucks, Detection of HBr and upper limit for HOBr: Bromine partitioning in the stratosphere, *Geophys. Res. Lett.*, *22*, 1373–1376, 1995.

Kavouras, I., N. Mihalopoulos, and E. Stephanou, Formation of atmospheric particles from organic acids produced by forests, *Nature*, *395*, 683–686, 1998.

Kegley Owen, C., M. Gilles, J. Burkholder, and A. Ravishankara, Rate coefficient measurements for the reaction $OH+ClO \longrightarrow products$, *J. Phys. Chem. A*, *103*, 5040–5048, 1999.

Khattatov, B. V., J. C. Gille, L. Lyjak, G. P. Brasseur, V. L. Dvortsov, A. E. Roche, and J. W. Waters, Assimilation of photochemically active species and a case analysis of UARS data, *J. Geophys. Res.*, *104*, 18,715–18,737, 1999.

Lary, D., Gas phase atmospheric bromine photochemistry, *J. Geophys. Res.*, *101*, 1505–1516, 1996.

Lary, D., Catalytic destruction of stratospheric ozone, *J. Geophys. Res.*, *102*, 21,515–21,526, 1997.

Lary, D., Data assimilation: A powerful tool for atmospheric chemistry, *Philosophical Transactions of the Royal Society, Series A, Mathematical, Physical and Engineering Sciences*, 1763, 1999.

Lary, D., and J. Pyle, Diffuse-radiation, twilight, and photochemistry: 1., *J. Atmos. Chem.*, *13*, 373–392, 1991a.

Lary, D., and J. Pyle, Diffuse-radiation, twilight, and photochemistry: 2., *J. Atmos. Chem.*, *13*, 393–406, 1991b.

Lary, D., and D. Shallcross, The potential importance of the reaction CO and HNO_3, *J. Geophys. Res.*, in press, 2000.

Lary, D., M. Chipperfield, J. Pyle, W. Norton, and L. Riishojgaard, 3-dimensional tracer initialization and general diagnostics using equivalent pv latitude-potential-

temperature coordinates, *Q. J. R. Meteorol. Soc.*, *121*, 187–210, 1995a.

Lary, D., M. Chipperfield, and R. Toumi, The potential impact of the reaction $OH+ClO \longrightarrow HCl+ O_2$ on polar ozone photochemistry, *J. Atmos. Chem.*, *21*, 61–79, 1995b.

McKeen, S., et al., The photochemistry of acetone in the upper troposphere: A source of odd-hydrogen radicals, *Geophys. Res. Lett.*, *24*, 3177–3180, 1997.

Meier, R., D. Anderson, and M. Nicolet, Radiation-field in the troposphere and stratosphere from 240-1000 nm. 1., General-analysis, *Planet. Space Sci.*, *30*, 923–933, 1982.

Menke, W., *Geophysical Data Analysis: Discrete Inverse Theory*, Academic, San Diego, Calif., 1984.

Middlebrook, A., D. Murphy, and D. Thomson, Observations of organic material in individual marine particles at Cape Grim during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, *103*, 16,475–16,483, 1998.

Muller, J., and G. Brasseur, Sources of upper tropospheric HO_x: A three-dimensional study, *J. Geophys. Res.*, *104*, 1705–1715, 1999.

Murphy, D., D. Thomson, and T. Mahoney, In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, *282*, 1664–1669, 1998.

Newchurch, M., et al., Stratospheric NO and NO_2 abundances from ATMOS solar-occultation measurements, *Geophys. Res. Lett.*, *23*, 2373–2376, 1996.

Nicolet, M., R. Meier, and D. Anderson, Radiation-field in the troposphere and stratosphere .2. Numerical-analysis, *Planet. Space Sci.*, *30*, 935–983, 1982.

Nolt, I., et al., Stratospheric HBr concentration profile obtained from far-infrared emission spectroscopy, *Geophys. Res. Lett.*, *24*, 281–284, 1997.

Novakov, T., and J. Penner, Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, *365*, 823–826, 1993.

Novakov, T., D. Hegg, and P. Hobbs, Airborne measurements of carbonaceous aerosols on the east coast of the united states, *J. Geophys. Res.*, *102*, 30,023–30,030, 1997.

Portmann, R., S. Brown, T. Gierczak, , R. Talukdar, J. Burkholder, and A. Ravishankara, Role of nitrogen ox-
ides in the lower stratosphere: A reevaluation based on laboratory studies, *Geophys. Res. Lett.*, *26*, 2387–2390, 1999.

Press, W., S. Teukolsky, W. Vetterling, and B. Flannery, *Numerical Recipes in Fortran - The Art of Scientific Computing*, 2nd ed., Cambridge Univ. Press, New York, 1992.

Sheridan, P., C. Brock, and J. Wilson, Aerosol-particles in the upper troposphere and lower stratosphere: Elemental composition and morphology of individual particles in northern midlatitudes, *Geophys. Res. Lett.*, *21*, 2587–2590, 1994.

Shevchenko, V., A. Lisitzin, V. Kuptzov, H. VanMalderen, J. Martin, R. VanGrieken, and W. Huang, Composition of aerosols in the marine boundary layer over the seas of the western Russian arctic, *Okeanologiya*, *39*, 142–151, 1999.

Stoer, J., and R. Bulirsch, *Introduction to Numerical Analysis*, Springer-Verlag, New York, 1980.

Vasconcellos, P., P. Artaxo, P. Ciccioli, A. Cecinato, E. Brancaleoni, and M. Frattoni, Chemical composition of aerosol collected in the Amazon forest, *Quim. Nova*, *21*, 385–393, 1998.

Wang, K., D. Lary, and S. Hall, Improvement of a 3D CTM and a 4D-VAR assimilation on a vector machine Cray J90 through a multitasking strategy, *Comp. Phys. Comm.*, *125*, 142–153, 2000.

WMO, Scientific assessment of ozone depletion: 1998, *Tech. Rep. 44*, WMO Global Ozone Res. and Monitor. Proj., Geneva, 1998.

D. J. Lary, Centre For Atmospheric Science, Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, CB2 1EW, England. (e-mail: david.lary@atm.ch.cam.ac.uk)

D. E. Shallcross, School of Chemistry, University of Bristol, Bristol, BS8 1TS, England, United Kingdom.