

## Photodissociation of acetone: Atmospheric implications of temperature-dependent quantum yields

S. R. Arnold and M. P. Chipperfield

Institute for Atmospheric Science, School of Environment, University of Leeds, Leeds, UK

M. A. Blitz, D. E. Heard, and M. J. Pilling

Department of Chemistry, University of Leeds, Leeds, UK

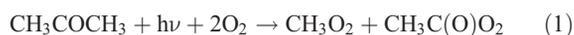
Received 18 November 2003; revised 1 March 2004; accepted 18 March 2004; published 13 April 2004.

[1] We have used a photochemical box model to investigate the effect of temperature-dependent quantum yields of acetone on the chemistry in the upper troposphere. The T-dependent quantum yields produce a photolysis (J) rate up to factor 3–10 slower than room temperature values. This reduced J rate significantly reduces the contribution of acetone to the mid-latitude and tropical UT HO<sub>x</sub> budgets by factors of 4 and 2 respectively, when constrained with location-specific aircraft observations. The calculated lifetime of acetone in the UT increases from ~75 to ~250 days at mid-latitudes and from ~10 to ~20 days in the tropics, for the conditions used here. This will significantly affect studies aimed at balancing the atmospheric acetone budget. Overall, these new quantum yields have large implications for our understanding of the role of acetone in the chemistry of the UT. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation. **Citation:** Arnold, S. R., M. P. Chipperfield, M. A. Blitz, D. E. Heard, and M. J. Pilling (2004), Photodissociation of acetone: Atmospheric implications of temperature-dependent quantum yields, *Geophys. Res. Lett.*, 31, L07110, doi:10.1029/2003GL019099.

### 1. Introduction

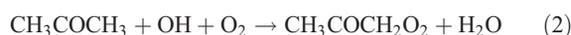
[2] Recent studies have indicated that acetone may play an important role in the chemistry of the upper troposphere (UT). Acetone photolysis can act as a source of HO<sub>x</sub>, peroxy and alkoxy radicals which can also change the partitioning of odd-nitrogen between NO<sub>x</sub> and reservoir species such as HONO<sub>2</sub> and peroxyacetyl nitrate (PAN) [e.g., Singh *et al.*, 1995; Arnold *et al.*, 1997; McKeen *et al.*, 1997]. However, these studies quantified the effect of acetone using temperature-independent quantum yields for acetone photodissociation.

[3] The atmospheric sinks for acetone are photolysis, reaction with OH and surface deposition. Photolysis occurs mainly through the initial formation of methyl peroxy and acetyl peroxy radicals:



Another minor photolysis channel (initially producing 2CH<sub>3</sub> and CO) is possible but its rate is many orders of magnitude

slower at wavelengths relevant to the UT. Reaction with OH can be represented by:



Photolysis of acetone occurs in the wavelength range 290–320 nm in the troposphere, so the rate of equation (1) increases with altitude. In contrast reaction (2) is more efficient in the moist lower troposphere. Moreover, photolysis can lead to a net production of 3.2 HO<sub>x</sub> molecules, while reaction with OH leads to a net production of up to 2 HO<sub>x</sub> molecules [Singh *et al.*, 1995]. Consequently, the relative importance of the different acetone sinks as a function of altitude has important implications for tropospheric chemistry.

[4] Recently, Blitz *et al.* [2004] presented the first measurements to show a temperature dependence for the acetone quantum yields. Their results indicate that at low temperatures typical of the UT, photolysis of acetone may be significantly (approximately a factor of 3.5 at summer mid-latitudes) slower than at room temperature. Clearly this difference is likely to reduce the calculated impact of acetone on tropospheric chemistry. In this paper we use a photochemical box model to compare the impacts of the new quantum yields (NQY) and the currently recommended (effectively temperature-independent) quantum yields (RQY) on UT photochemistry.

### 2. Photochemical Model and Experiments

[5] We have used the CiTTYCAT 0-D photochemical box model [Evans *et al.*, 2000], which comprises a detailed gas-phase tropospheric chemistry, and to which we have added an acetone photo-oxidation scheme. Photolysis of photo-labile species in the model is treated using the isotropic two-stream approach of Hough [1988]. New yields (NQY) are included using the parameterisation of Blitz *et al.* [2004], while the recommended yields (RQY) are taken from Warneck [2001], as recommended by IUPAC 2002 [Atkinson *et al.*, 2002]. Acetone absorption cross-sections are taken directly from Gierczak *et al.* [1998]. The rate constant for the reaction of acetone with OH is taken from a 2003 update to the IUPAC 2002 recommendation [http://www.iupac-kinetic.ch.cam.ac.uk/], which has  $k = 8.8 \times 10^{-12} \exp(-1320/T) + 1.7 \times 10^{-14} \exp(420/T)$ . A seasonally averaged cloud field is included in the photolysis calculations [Hough, 1988].

[6] The impact of the new yields has been investigated in a series of 3 model experiments (summarised in Table 1).

**Table 1.** Prescribed Chemistry and Conditions for UT Model Experiments

Description	Exp 1a	Exp 1b	Exp 2	Exp 3
	Constrained Background		Initialised Convective	Convective Mixing
Latitude	50°N	0°N	50°N	0°N
Pressure/hPa	287	230	262	230
Temperature/K	222	225	220	226
H <sub>2</sub> O/kgkg <sup>-1</sup>	7.5 × 10 <sup>-5</sup>	9.4 × 10 <sup>-6</sup>	8.0 × 10 <sup>-5</sup>	6.25 × 10 <sup>-5</sup>
Acetone/pptv	510	250	560	600
NO/pptv	56	58	443	10–6000
NO <sub>2</sub> /pptv	30	–	163	–
O <sub>3</sub> /ppbv	55	36	55	20
CO/ppbv	90	60	92	60
CH <sub>4</sub> /ppmv	1.761	1.720	1.761	1.700
PAN/pptv	64	–	55	–
HONO <sub>2</sub> /pptv	120	–	130	–
HO <sub>2</sub> NO <sub>2</sub> /pptv	60	–	63	–
C <sub>2</sub> H <sub>6</sub> /pptv	670	–	720	–
C <sub>3</sub> H <sub>8</sub> /pptv	79	–	110	–
C <sub>2</sub> H <sub>2</sub> /pptv	91	–	110	–
C <sub>6</sub> H <sub>6</sub> /pptv	15	–	14	–
H <sub>2</sub> O <sub>2</sub> /pptv	–	–	–	50
CH <sub>3</sub> OOH/pptv	–	–	–	50

These cover situations where the chemistry is constrained by observations of acetone (and other species) and situations where the model acetone is free to evolve. More details of the individual model runs are given in the relevant Results section. The constrained model experiments were run over a perpetual 24-hour period until a repeatable diurnal cycle was reached.

### 3. Model Results

[7] *Blitz et al.* [2004] presented profiles of photolysis rates using the recommended and new yields. The temperature-dependent NQY produced J rates a factor  $\sim 3$ –10 slower than the RQY in the cold UT. Here we investigate the chemical implications of such a large decrease in acetone photolysis.

#### 3.1. Experiment 1: Constrained Model

[8] To investigate the impact of NQY on a chemical system typical of the UT, the model was constrained using observations of UT concentrations for mid-latitude (Exp. 1a) and tropical (Exp. 1b) conditions. Species were constrained to their observed concentrations (Table 1) every 5-minute model time step. NO<sub>y</sub> species were constrained every 24hrs to allow the model to diagnose chemical diurnal cycles over the course of a day. H<sub>2</sub>O<sub>2</sub>, HCHO, HO<sub>2</sub> and OH were allowed to run freely in the simulation.

[9] Experiment 1a uses mid-latitude observations from the background UT made during the SONEX experiment [*Jaeglé et al.*, 2000]. The box was situated at  $\sim 10$  km, at 50°N, on October 28 to coincide with the approximate location and median time of the observations. Table 2 shows the results of this experiment. Steady-state HO<sub>x</sub> concentrations calculated by the constrained model are shown as diurnal mean values. HO<sub>x</sub> increases due to acetone are significantly reduced by the slower J rate given by NQY. OH and HO<sub>2</sub> increases of approximately 35% and 45% with the introduction of acetone, are reduced to increases of about 9% and 11% respectively. The steady state lifetime of acetone in the mid-latitude background UT is significantly

**Table 2.** Steady State Day Averages From Box Model Constrained by Midlatitude UT Observations (Experiment 1a)

	No Acetone	RQY	NQY
OH/pptv	0.019	0.026	0.021
HO <sub>2</sub> /pptv	0.48	0.70	0.54
Acetone loss J/s <sup>-1</sup>		1.23 × 10 <sup>-7</sup>	1.94 × 10 <sup>-8</sup>
Acetone loss $k_2$ [OH]/s <sup>-1</sup>	1.90 × 10 <sup>-8</sup>	3.27 × 10 <sup>-8</sup>	2.62 × 10 <sup>-8</sup>
Propane loss $k$ [OH]/s <sup>-1</sup>	1.01 × 10 <sup>-7</sup>	1.36 × 10 <sup>-7</sup>	1.09 × 10 <sup>-7</sup>
Acetone lifetime		74 days	254 days

increased from  $\sim 75$  days to  $\sim 255$  days. The reduction in calculated HO<sub>x</sub> concentrations suggests that further contributions from HO<sub>x</sub> sources in addition to acetone are required for basic NMHC-NO<sub>x</sub>-HO<sub>x</sub> chemistry schemes to reproduce the magnitudes of tropospheric HO<sub>x</sub> abundances.

[10] For tropical UT conditions, Experiment 1b takes values from a compilation of observations in the North and South tropical Pacific [*Crawford et al.*, 1999]. The model was run at an altitude of  $\sim 11$  km at the Equator. Results are presented in Table 3. Acetone induced OH and HO<sub>2</sub> increases of approximately 40% and 63%, are reduced to increases of about 22% and 29% respectively, with the steady-state lifetime of acetone increasing from  $\sim 9$  to  $\sim 21$  days. The impact of acetone on HO<sub>x</sub> is greater than for the mid-latitude SONEX conditions, due to the dry tropical UT environment where the O(<sup>1</sup>D) + H<sub>2</sub>O primary source is smaller. The NQY J rate therefore plays a significant role in reducing steady-state HO<sub>x</sub> concentrations under these conditions, despite a smaller reduction to the J rate itself than seen at mid-latitudes.

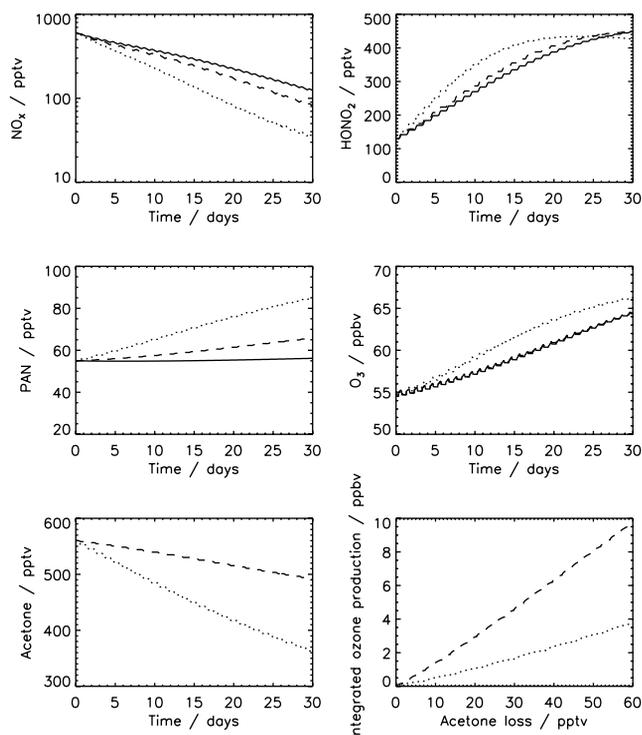
[11] It should be noted that the calculated changes to lifetimes and chemistry are dependent on the specific conditions and locations chosen. Nevertheless, the two contrasting latitudes used illustrate the potential impact of the NQY on tropospheric chemistry.

#### 3.2. Experiment 2: Free-Running Model

[12] To allow the chemical model to respond to an increase in acetone above background in the UT, the model was allowed to run freely after initialisation with observations of median UT concentrations from air masses with influence from continental convection intercepted during the SONEX experiment (see Table 1). This simulates the evolution of a freshly polluted isolated air parcel having been injected to the UT in a convective updraught. The box altitude was set with the median pressure of convectively influenced observations. Chemistry was allowed to run freely for 30 perpetual days, simulating an assumed isolation of the air mass in the UT over that period.

**Table 3.** Steady State Day Averages From Box Model Constrained by Tropical UT Observations (Experiment 1b)

	No Acetone	RQY	NQY
OH/pptv	0.069	0.097	0.084
HO <sub>2</sub> /pptv	1.46	2.38	1.89
Acetone loss J/s <sup>-1</sup>		1.22 × 10 <sup>-6</sup>	4.81 × 10 <sup>-7</sup>
Acetone loss $k_2$ [OH]/s <sup>-1</sup>	6.84 × 10 <sup>-8</sup>	9.70 × 10 <sup>-8</sup>	8.34 × 10 <sup>-8</sup>
Propane loss $k$ [OH]/s <sup>-1</sup>	2.97 × 10 <sup>-7</sup>	4.22 × 10 <sup>-7</sup>	3.63 × 10 <sup>-7</sup>
Acetone lifetime		9 days	21 days



**Figure 1.** Comparison of chemical responses to the injection of a convective plume of fresh acetone into the UT for the recommended acetone quantum yields (RQY, dotted) and the new acetone quantum yields (NQY, dashed). A base run without acetone is shown by the solid curves.

[13] Results from this experiment are shown in Figure 1. The slower production of peroxy radicals given by the reduced NQY acetone loss rate results in a reduction in the enhancement to ozone production seen when introducing acetone to the system. The reduced acetone loss also produces a slower conversion of  $\text{NO}_x$  to PAN and  $\text{HONO}_2$ , through reductions in peroxyacetyl and  $\text{HO}_x$  formation. The result is that  $\text{NO}_x$  concentrations are maintained for longer in the fresh convective plume. As a consequence, the ozone production efficiency per molecule of acetone lost increases with the NQY. Figure 1 demonstrates that integrated ozone production rates for NQY and RQY are  $\sim 0.17$  ppbv and  $\sim 0.06$  ppbv ozone per pptv acetone loss respectively.

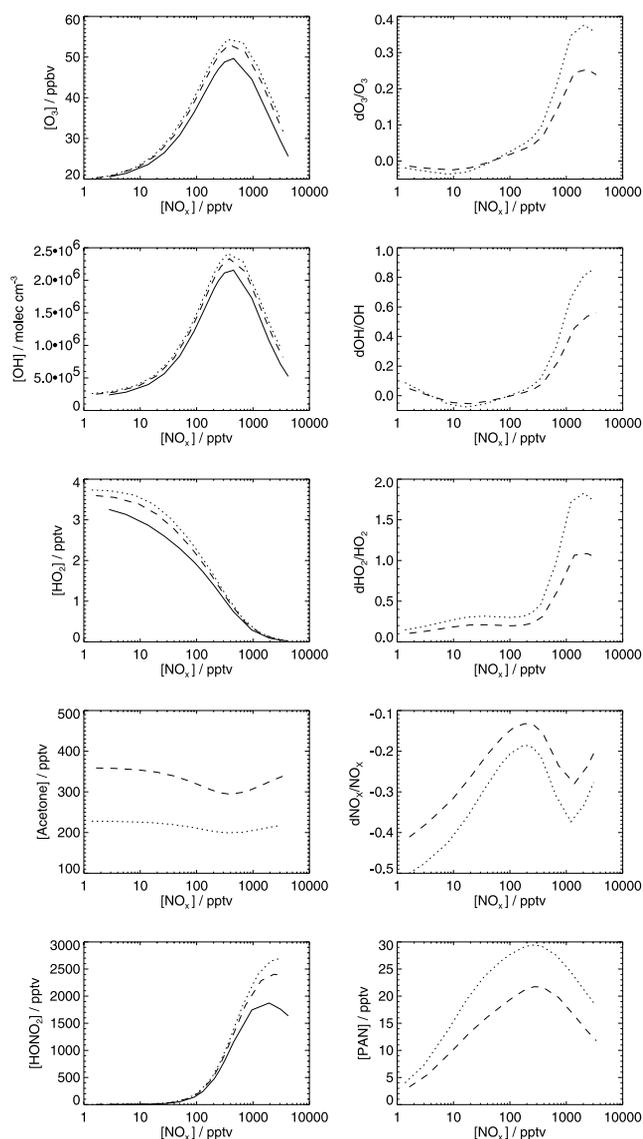
[14] Note that this result is affected by the lack of transport in the model. Conversion of  $\text{NO}_x$  to PAN and preservation of the PAN that is formed, are facilitated by the air mass remaining at cold temperatures in the UT. However, the result highlights a shift in the speciation of  $\text{NO}_y$  and ozone production in the UT resulting from the NQY.

### 3.3. Experiment 3: Convective Outflow Into UT

[15] This model experiment is designed to give a more realistic treatment of the impact of a convective influx of freshly polluted air to the UT. We have repeated the box model experiments of *Folkins and Chatfield* [2000], using a model set up without acetone, with acetone and NQY, and with acetone and RQY. The experiment simulates the chemical response of the UT to a steady-state replacement of air in the UT by fresh convective outflow, with varying concentrations of  $\text{NO}_x$ . Table 1 shows the concentra-

tions used for the incoming convective air.  $\text{NO}$  was varied between 0.01 and 6.0 ppbv. Following *Folkins and Chatfield* [2000], the box was situated at a temperature of 226K at 230 hPa in the tropical UT, and air was continuously replaced in the box by fresh ‘convective influx’ on a 15-day timescale. The model was run for each concentration of incoming  $\text{NO}_x$  and for each acetone photolysis set-up for 110 perpetual days to allow a steady state to be reached between chemistry and mixing. Note that the updated acetone + OH rate constant and the most recently recommended acetone quantum yields RQY are different from those used in the original study of *Folkins and Chatfield* [2000].

[16] The effect of varying  $\text{NO}_x$  in the incoming convective air is shown in Figure 2. The fractional increase in  $\text{HO}_x$



**Figure 2.** Comparison of the UT chemical response to steady-state continuous convective outflow into the UT as a function of ambient  $\text{NO}_x$  for recommended acetone quantum yields (RQY, dotted) and the new acetone quantum yields (NQY, dashed). Solid curves in the left panels show a baseline run with no acetone included.

with the introduction of acetone is seen to be greatest at high  $\text{NO}_x$ , where the photo-oxidation route of acetone is most efficiently taken to completion [Singh *et al.*, 1995; Folkins and Chatfield, 2000]. However, the NQY reduce this maximum increase to approximately +55% OH and +95%  $\text{HO}_2$  from approximately +85% OH and +170%  $\text{HO}_2$ . Above 100 pptv of  $\text{NO}_x$ , ozone and  $\text{HO}_x$  are increased by the addition of acetone and PAN formation is maximised. These increases are suppressed by NQY, with a reduction in maximum PAN production of approximately 30%. The maximum increase to ozone production with the introduction of acetone occurs at around 1 ppbv  $\text{NO}_x$ , where radical conversion of NO to  $\text{NO}_2$  is most efficient. At high  $\text{NO}_x$ , where  $\text{HO}_x$  production from acetone is maximised, increases in ozone production decrease due to enhanced formation of  $\text{HONO}_2$ . The NQY reduce the maximum enhancement in ozone from approximately +35% to +20%, while increases in  $\text{HONO}_2$  are reduced from about +30% to about +20%. Our range of steady-state acetone concentrations is increased from 200–230 pptv to 300–370 pptv when using the new yields. As noted previously, the NQY mean that the loss of acetone to OH and photolysis are of a more similar magnitude. This is also evident from the enhanced reduction in steady-state acetone concentration at the  $\text{NO}_x$  concentration which maximises OH.

[17] It is interesting to compare the results of this experiment with Experiment 2. The continuous replacement of fresh  $\text{NO}_x$  in the incoming convective air means that the production of PAN is not a hindrance to enhanced ozone production from acetone. However, at very low  $\text{NO}_x$  ozone production is reduced as loss of  $\text{NO}_x$  to PAN outweighs any increase in  $\text{HO}_2$  from acetone, as observed by Folkins and Chatfield [2000].

#### 4. Discussion and Conclusions

[18] The new quantum yields (NQY) for acetone photolysis have been shown to make significant differences to the chemical perturbations resulting from the introduction of acetone into the UT at both mid-latitudes and in the tropics. For the specific conditions used, the steady-state lifetime of acetone diagnosed from a box model constrained with observed UT concentrations increases from about 75 to 250 days at mid-latitudes and from 9 to 21 days in the tropical UT. Increases in background  $\text{HO}_x$  due to acetone are reduced by a factor of  $\sim 4$  at mid-latitudes and by a factor of  $\sim 2$  in the tropics. The tropical conditions used here mean that a 30% contribution by acetone to the total OH concentration is reduced to 18%. At mid-latitudes, the example constraints used suggest a reduction in the acetone contribution to OH from 25% to 8%.

[19] With NQY, PAN formation in the model is significantly reduced, which has been shown to have implications for the efficiency of ozone production from acetone in the UT. These results suggest that an isolated injection of acetone and  $\text{NO}_x$  into the UT may result in less storage of  $\text{NO}_x$  in the reservoir species PAN, than would have been suggested by using RQY. Regular replacement of air in the UT by fresh acetone and  $\text{NO}_x$  allows efficient ozone production despite more efficient  $\text{NO}_x$  loss to PAN with RQY, since enough  $\text{NO}_x$  is replenished to maintain ozone

production. Under such conditions, the enhancement to UT ozone is reduced by NQY. These issues are likely to have implications for the large-scale distribution of reactive  $\text{NO}_y$  and ozone in the troposphere, and should be examined further using a 3D chemical transport model.

[20] The large increases in the acetone lifetime have been deduced under UT conditions, where the NQY show a maximum departure from RQY [Blitz *et al.*, 2004]. However, the effects of the NQY are likely to have important implications for the global troposphere. Longer transport timescales for acetone in the UT may help reconcile previously unexplained abundances of acetone in the UT remote from source regions. Acetone budget studies [e.g., Jacob *et al.*, 2002] will need to re-address the source terms required to balance a greater acetone lifetime. The reduced  $\text{HO}_x$  yield from acetone in the UT also suggests that additional  $\text{HO}_x$  sources must be sought in order to balance UT  $\text{HO}_x$  budgets [e.g., Jaeglé *et al.*, 2000].

[21] **Acknowledgments.** SRA thanks the UK Natural Environment Research Council (NERC) for a studentship. We thank two anonymous referees for useful comments.

#### References

- Arnold, F., V. Burger, B. Droste-Fanke, F. Grimm, A. Krieger, J. Schneider, and T. Stilp (1997), Acetone in the upper troposphere and lower stratosphere: Impact on trace gases and aerosols, *Geophys. Res. Lett.*, **24**, 3017–3020.
- Atkinson, R., et al. (2002), Summary of evaluated kinetic and photochemical data for atmospheric chemistry, *Data Sheet P7*, Int. Union of Pure and Appl. Phys., London.
- Blitz, M. A., D. E. Heard, M. J. Pilling, S. R. Arnold, and M. P. Chipperfield (2004), Pressure and temperature-dependent quantum yields for the photodissociation of acetone between 279 and 327.5 nm, *Geophys. Res. Lett.*, **31**, L06111, doi:10.1029/2003GL018793.
- Crawford, J., et al. (1999), Assessment of upper tropospheric  $\text{HO}_x$  sources over the tropical Pacific based on NASA GTE/PEM data: Net effect on  $\text{HO}_x$  and other photochemical parameters, *J. Geophys. Res.*, **104**, 16,255–16,273.
- Evans, M. J., et al. (2000), Evaluation of a Lagrangian box model using field measurements from EASE (Eastern Atlantic Summer Experiment) 1996, *Atmos. Environ.*, **34**, 3843–3863.
- Folkins, I., and R. Chatfield (2000), Impact of acetone on ozone production and OH in the upper troposphere at high  $\text{NO}_x$ , *J. Geophys. Res.*, **105**, 11,585–11,599.
- Gierczak, T., J. B. Burkholder, S. Bauerle, and A. R. Ravishankara (1998), Photochemistry of acetone under tropospheric conditions, *Chem. Phys.*, **231**, 229–244.
- Hough, A. M. (1988), The calculation of photolysis rates for use in global tropospheric modelling studies, *AERE Rep. R-13259*, Her Majesty's Stn. Off., Norwich, UK.
- Jacob, D. J., B. D. Field, E. M. Jin, I. Bey, Q. Li, J. A. Logan, R. M. Yantosca, and H. B. Singh (2002), Atmospheric budget of acetone, *J. Geophys. Res.*, **107**(D10), 4100, doi:10.1029/2001JD000694.
- Jaeglé, L., et al. (2000), Photochemistry of  $\text{HO}_x$  in the upper troposphere at northern midlatitudes, *J. Geophys. Res.*, **105**, 3877–3892.
- McKeen, S. A., et al. (1997), The photochemistry of acetone in the upper troposphere: A source of odd-hydrogen radicals, *Geophys. Res. Lett.*, **24**, 3177–3180.
- Singh, H. B., M. Kanakidou, P. J. Crutzen, and D. J. Jacob (1995), High concentration and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature*, **378**, 50–54.
- Warneck, P. (2001), Photodissociation of acetone in the troposphere: An algorithm for the quantum yield, *Atmos. Environ.*, **35**, 5773–5777.

S. R. Arnold and M. P. Chipperfield, School of the Environment, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK. (sra@env.leeds.ac.uk)

M. A. Blitz, D. E. Heard, and M. J. Pilling, Department of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK.