Vertical Profiles of Ethane and Propane in the Stratosphere

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Stratospheric measurements of the C_2H_6 mixing ratio up to 30 km and of the C_3H_8 mixing ratio up to 18 km altitude are reported. The observed vertical gradient of C_2H_6 is much weaker than that calculated from a one-dimensional steady state model, indicating lower concentrations of atomic chlorine in the lower stratosphere than those predicted by models. From the measured C_2H_6 profile a tentative estimate for the Cl concentration is derived.

INTRODUCTION

Balloon-borne cryogenic collection provides relatively large samples (10 l STP) of uncontaminated stratospheric air. This facilitates the simultaneous measurement of a large number of trace gases to high stratospheric altitudes. We have now extended our program to include the measurement of light non-methane hydrocarbons, C_2 to C_5, and we report here our first measurements of ethane, C_2H_6, and propane, C_3H_8, in the stratosphere.

The tropospheric background mixing ratios of both are quite low, about 2 ppb for C_2H_6 and less than 1 ppb for C_3H_8 [*Rudolph et al.*, 1979]. The fluxes of these gases into the stratosphere are small, and their impact on the stratospheric carbon and hydrogen budget is negligible. Nevertheless, C_2H_6 reacts rapidly with Cl atoms, and its presence should significantly decrease the Cl atom concentration in the lower stratosphere [*Aikin et al.*, 1979]. Furthermore, already the first model calculations [*Chameides and Cicerone*, 1978] indicated that the reaction with Cl atoms is by far the dominant loss mechanism of C_2H_6 in the stratosphere. Hence its vertical distribution should be controlled by the vertical distribution of the Cl concentration. Consequently, measured profiles of C_2H_6 could serve as a convenient method for determination of the vertical profile of Cl atoms in the lower stratosphere, a region where direct observations of Cl are not yet feasible. Here we use our present C_2H_6 profiles to derive an estimate for the Cl concentration in the lower stratosphere.

EXPERIMENTAL PROCEDURES

The stratospheric air samples were collected by a balloon-borne cryosampler similar to the design developed by *Lueb et al.* [1975]. The sampling procedures have been presented elsewhere [*Fabian et al.*, 1979a]. The tropospheric air samples were collected aboard an aircraft by grab sampling in electropolished stainless steel containers of 2-l volume. After return to the laboratory the air samples of 1–5 l STP were analyzed for their hydrocarbon content using a specially equipped gas chromatograph: The hydrocarbons are first enriched on a precolumn packed with Spherosil and Carbosieve B and cooled to temperatures of about 150 K, then thermally desorbed and separated on a column packed with Spherosil XOB 075 (6 m long and 0.8 mm inner diameter), and finally detected with a flame ionization detector. The gas chromatographic measurements were calibrated with standard mixtures of 0.5–3 ppb of C_2H_6 and C_3H_8 in synthetic air, which were prepared by three-step dilution in a static dilution system. The detection limits depended on actual sample size and were 2

ppt for C_2H_6 at 30 km altitude and 10 ppt for C_3H_8 at 18 km altitude. The errors of the gas chromatographic measurement are 10% for tropospheric mixing ratios; they increase to a factor 2 for samples with mixing ratios near the detection limit.

RESULTS

The stratospheric data were obtained from two balloon flights over southern France at 44°N on June 16 and 28, 1979. The tropospheric samples were collected during an aircraft flight on June 16, 1979. The sampling was part of a joint project for the measurement of stratospheric trace gases by the Kernforschungsanlage Jülich, the Max-Planck-Institut für Aeronomie in Lindau, and the Max-Planck-Institut für Chemie in Mainz. In addition to C_2H_6 and C_3H_8 the tropospheric samples also showed measurable concentrations of C_2H_4, C_2H_2, n-C_4H_{10}, i-C_4H_{10}, n-C_5H_{12}, and i-C_5H_{12}. Only C_2H_2, C_2H_6, and C_3H_8 could be detected in stratospheric air samples above 15 km altitude.

The C_3H_8 and C_2H_6 data are summarized in Figures 1 and 2. The measured C_3H_8 mixing ratio decreases extremely fast with altitude above the tropopause (11 km). Above 18 km altitude it is already below the detection limit of 10 ppt.

The measured stratospheric C_2H_6 mixing ratios (Figure 2) exhibit a similar rapid decrease with altitude. Because of its higher tropospheric mixing ratio, 2 ppb, and a lower detection limit, 2 ppt, the C_2H_6 can be observed to about 30 km altitude. Between the tropopause and 30 km the C_2H_6 mixing ratio drops more or less steadily by 3 orders of magnitude. However, the uppermost samples, although collected during descent, show elevated C_2H_6 mixing ratios for both flights. This is a clear indication of C_2H_6 contamination. Since the other trace gases measured for these flights do not show such a reversal in the vertical gradient, the elevated C_2H_6 concentration cannot be ascribed to stratospheric transport.

There are various steps in the sample collection and handling procedures at which contamination can occur: (1) leakage in the vacuum lines used for sample transfer, (2) leakage through the valves of the sample containers during storage, (3) outgassing of the various sample containers, (4) outgassing from the inner walls of the cryogenic sampler during collection (e.g., inlet line), and (5) outgassing from the external surfaces of balloon and payload during sample collection. Points 1 and 2 can be excluded with some certainty: Leakage would admix tropospheric air to the stratospheric samples and would cause contamination in all trace gases with high tropospheric-stratospheric concentration differences. This has not been observed. Point 3, C_2H_6 outgassing of the sample containers, seems to be negligible, as shown by blank experiments. This
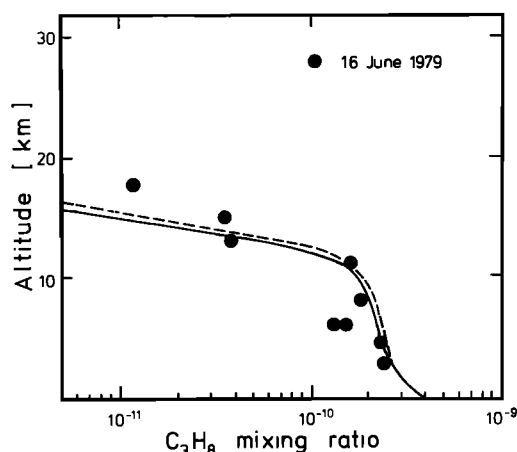
Fig. 1. Vertical profile of the C_3H_8 mixing ratio measured in the lower stratosphere over southern France, 44°N latitude. Solid and dashed curves represent model-predicted C_3H_8 profiles.

leaves internal or external outgassing of C_2H_6 in flight as most likely sources of contamination.

Indeed, samples from a balloon flight in November 1979 over southern France, which had to be collected during ascent rather than descent because of limited flight time, showed substantially higher mixing ratios of C_2H_6 and C_3H_8 than those presented here, especially above 20 km altitude. This strongly indicates in-flight contamination. These data also indicate that the C_2H_6 outgassing rate drops rapidly with time, about an order of magnitude per hour.

Having narrowed the likely sources to in-flight contamination, we can try to estimate its extent. The sample collection rate of the cryosampler is inversely proportional to the square of the air pressure p [*Lueb et al.*, 1975, Figure 3]. Thus in the case of internal contamination the ratio of contamination rate to sampling rate will decrease with decreasing sampling altitude at least as $1/p^2$ even if we admit a constant outgassing rate. In the case of external outgassing the released contamination will be diluted with surrounding air of pressure
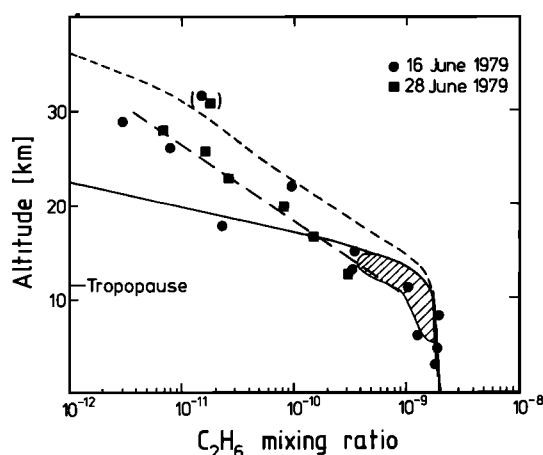

Fig. 2. Vertical profiles of the C_2H_6 mixing ratio in the stratosphere over southern France, 44°N latitude. The dash-dotted line represents a least squares fit of an exponential profile to the data excluding the data in parentheses, which are obviously contaminated. The hatched area shows the range of data by *Cronn and Robinson* [1979a]. The solid curve represents the C_2H_6 profile predicted by a one-dimensional steady state model. The dashed curve is a prediction neglecting reaction of C_2H_6 with Cl.

p, and the contamination will decrease with decreasing altitude at least as $1/p$. An estimate of contamination decreasing as $1/p$ with altitude based on the assumption of external outgassing with constant rate will therefore be rather conservative.

Applying this estimate to the actual flights and assuming that the C_2H_6 measured in the samples at the second highest altitudes (28.9 and 27.9 km, respectively) were completely caused by contamination, the next lowest samples (26 km) would have a contribution by contamination of less than 30%, and the lower samples of less than 10%. The latter value is less than the precision of the gas chromatographic measurement. This rapid falloff in contamination with decreasing altitude is also indicated by the rapid drop of a factor of 2–4 in mixing ratio between the highest and next highest samples observed during the flights in June 1979 (Figure 2). Although there remains an element of uncertainty until the actual source of contamination is identified and removed, it appears safe to assume that the C_2H_6 mixing ratios at and below 26 km are little affected by contamination.

The stratospheric data points shown in Figure 2 fall essentially on a straight line. Since contamination below 30 km altitude is small, the measured decrease in C_2H_6 mixing ratio is virtually exponential, certainly up to 26 km altitude and possibly up to 30 km altitude. A least squares fit gives a scale height of 3.5 ± 0.15 km for the decrease. It was calculated excluding the contaminated samples above 30 km and the two straggling points at 18 and 22 km altitude from the profile on June 16, 1978. The fitted exponential decrease is also shown in Figure 2 (dash-dotted line).

DISCUSSION

Very few published data covering the lower stratosphere and upper troposphere are available for comparison. We could not find any other C_3H_8 measurements for that altitude range in the literature, and for C_2H_6 the only measurements published seem to be those of *Cronn and Robinson* [1979a, b]. These authors measured the C_2H_6 mixing ratio in about 60 samples collected aboard an aircraft over the San Francisco Bay area (37°N) during April 1977 at altitudes ranging mostly from 2 km below to 3 km above the tropopause [*Cronn and Robinson*, 1979a]. The tropopause altitude ranged between 11.3 and 12 km. Despite a considerable scatter, which the authors ascribed partly to the experimental imprecision, the data showed a clear and steep decrease of the C_2H_6 mixing ratio in the lower stratosphere. To avoid confusion, only the range of the C_2H_6 values by *Cronn and Robinson* [1979a] is indicated in Figure 2 by the hatched area. The present data fall well within that range, indicating reasonable agreement in the absolute calibration.

The rapid decrease in the C_2H_6 mixing ratio observed by *Cronn and Robinson* [1979a] in the lower stratosphere is confirmed and extended to higher altitudes by our measurements. It is due to the fast destruction of C_2H_6 by Cl atoms and OH radicals:
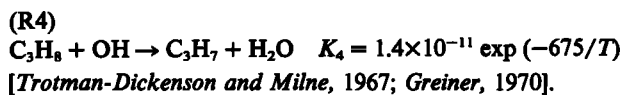
(R1)
$$C_2H_6 + Cl \rightarrow C_2H_5 + HCl \quad K_1 = 7.3 \times 10^{-11} \exp\,(-61/T)$$

(R2)
$$C_2H_6 + OH \rightarrow C_2H_5 + H_2O \quad K_2 = 1.86 \times 10^{-11} \exp\,(-1230/T)$$

[*Manning and Kurylo*, 1977; *Greiner*, 1970].

Similarly, C_3H_8 is destroyed by the reactions

(R3)

$C_3H_8 + Cl \rightarrow C_3H_7 + HCl$ $K_3 = 3.2 \times 10^- \exp(-340/T)$

(R4)

$C_3H_8 + OH \rightarrow C_3H_7 + H_2O$ $K_4 = 1.4 \times 10^{-11} \exp(-675/T)$

[*Trotman-Dickenson and Milne*, 1967; *Greiner*, 1970].

At stratospheric temperatures the rate constants for the reaction with Cl are much faster than those for reaction with OH. Thus reaction with Cl is a significant or even the dominant loss path in both cases, despite the fact that the stratospheric concentrations of Cl are much lower than those of OH. On the basis of model-calculated vertical profiles of Cl and OH concentration (cf. Figure 3), 90% of the stratospheric destruction of C_2H_6 is due to reaction with Cl.

Because of its fast reaction with Cl atoms the presence of C_2H_6 tends to lower the Cl concentration at those stratospheric altitudes where C_2H_6 is still present in significant mixing ratios [*Aikin et al.*, 1979]. This is also demonstrated in Figure 3 by the Cl profiles predicted from our one-dimensional (1-D) steady state model of stratospheric chemistry: Below 18 km altitude the Cl profile influenced by C_2H_6 (dash-dotted curve) falls significantly below the Cl profile, which neglects the presence of C_2H_6 (solid curve). The maximum reduction of about a factor of 3 is reached around the tropopause. Owing to the steep decrease of C_2H_6 in the model, its influence on the Cl profile above 18 km is negligible.

The presence of C_3H_8 also reduces the Cl concentration. The reduction is largest around the tropopause, about 40%, and drops rapidly with increasing altitude. Above 14 km altitude the effect is negligible. The effect of C_3H_8 is not included in the Cl profiles shown in Figure 3.

The Cl and OH profiles in Figure 3 were calculated for spring, 45°N latitude, and a tropopause altitude of 11 km, in order to match the average solar flux, temperature, and transport conditions prevailing during the time of sample collection. They are diurnally averaged. The total chlorine mixing ratio (Cl, ClO, ClONO$_2$, and HCl) in the model is 2.5 ppb at 30 km altitude. The model utilizes the chemistry and rate constants described by *Hudson and Reed* [1979]. The details have been described elsewhere [*Röth et al.*, 1980]. Both Cl and OH profiles compare favorably with those predicted by other 1-D models using similar chemistry [cf. *Chameides and Cicerone*, 1978; *National Academy of Sciences*, 1979; J. S. Chang, private communication, 1979].

The model calculations also predicted the C_2H_6 and C_3H_8 profiles at 45°N. The above reactions were the only destruction paths included for the higher hydrocarbons; reaction with O^1D remains negligible. There are no known production mechanisms for C_2H_6 in the stratosphere. The boundary conditions at the ground were based on measured mixing ratios at mid-latitudes: 2 ppb for C_2H_6 and 0.4 ppb for C_3H_8. The predicted profiles are also included in Figures 1 and 2 (solid curves). In order to demonstrate the importance of the reaction with Cl atoms, profiles neglecting the Cl reactions, (R1) and (R3), were also calculated (dashed curves).

The C_3H_8 data (Figure 1) are too few at present to warrant detailed investigation; nevertheless, within the observed scatter and experimental error the data and predicted profiles seem to agree.

The C_2H_6 data are much more interesting in the sense that they show a significant and systematic deviation over a large altitude range from the rapid decrease predicted by the 1-D steady state model. The deviation is rather large: At 20 km al-
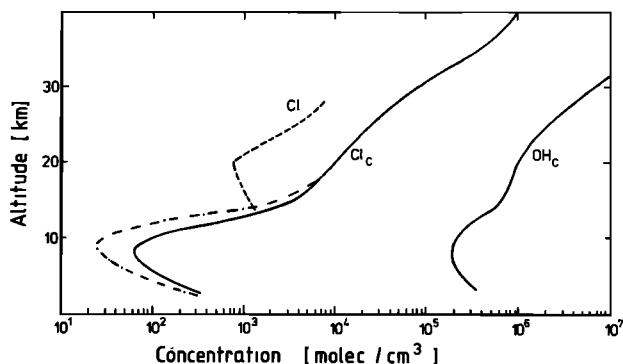

Fig. 3. Vertical profiles of Cl atom and OH radical concentrations in the stratosphere. The profiles Cl_c and OH_c were calculated from a one-dimensional steady state model. The calculated Cl profile changes to the dash-dotted curve when the presence of C_2H_6 is taken into account. The upper limit for the Cl concentration estimated from the measured C_2H_6 data is given by the dashed curve.

titude the measured mixing ratio is 1 order of magnitude higher and at 25 km altitude, 2 orders of magnitude higher than the model-calculated values. Such a comparison could be questioned. The model, whose transport has been reduced to simple vertical eddy diffusion, constructs a temporally and horizontally averaged profile, whereas the experimental profiles are subject not only to temporal variations in the local C_2H_6 mixing ratio but also to fluxes, which can have vertical and horizontal, turbulent and advective components. It is likely that the measured C_2H_6 data do deviate to some extent from the local average, certainly from the global average as it is defined by a 1-D model. The question is whether a local and temporary transport perturbation can enhance the C_2H_6 mixing ratio by as much as is observed here. If not, we have to admit the possibility of a lower stratospheric destruction rate of C_2H_6.

To that end, the various models of transport need to be discussed and checked against the available information. We first note that the experimental data consist of two sets which, although sampled about 2 weeks apart, superimpose quite well to form the same general profile. The temporal variations were small at most altitudes. On the other hand the model-calculated lifetimes of C_2H_6 for chemical destruction, τ_c, is short. It decreases from 20 days at 20 km altitude to 2 days at 30 km altitude (Figure 4). Thus if the profile collected on June 16, 1979, had been due to a momentary perturbation of the modeled average profile, the mixing ratios in the upper part should have relaxed toward that average profile by June 28, 1979, when the next profile was collected. Such a relaxation was not observed. Either stratospheric destruction of C_2H_6 was much slower than was predicted by the model, or it was matched by a large divergence of the C_2H_6 flux. In any case the transport pattern which established and maintained the measured C_2H_6 profile must have persisted longer than the C_2H_6 lifetime at the higher altitudes, at least for a few weeks.

With that, one mode of transport can be dismissed as unlikely. Transport by a mean vertical wind component would require velocities around 2 cm/s at 30 km and 0.5 cm/s at 25 km altitude to maintain the observed C_2H_6 profile against a destruction characterized by τ_c. Persistence of that mode for several weeks would push the mixing ratios of the longer-lived trace gases CH_4, N_2O, CF_2Cl_2, and $CFCl_3$ at 25 or 30 km alti-
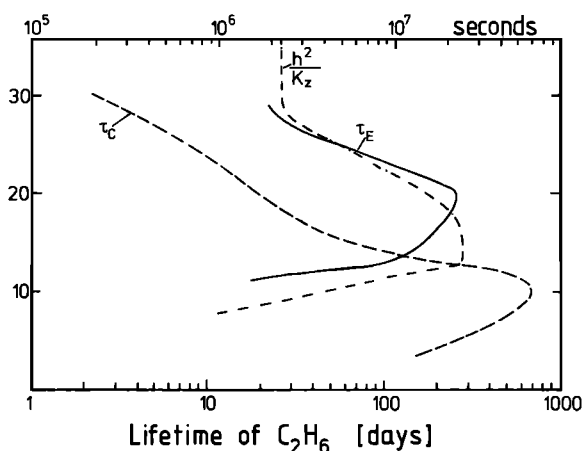
Fig. 4. Vertical profile of the C_2H_6 lifetime in the stratosphere: τ_c represents the model prediction, and τ_E is derived from the measured C_2H_6 profile. The leading term of τ_E, h^2/K_z, is also shown.

tude to much higher values than were actually observed in the present flights [*Fabian et al.*, 1979b].

Increased vertical eddy diffusion is not so readily dismissed. In this case, which implies vertical mixing, the time with which the profile responds to a change in transport rate depends on the chemical lifetime of the molecule considered. Since C_2H_6 is much shorter lived, its profile might have approached a form such as that measured without a noticeable, simultaneous change in the measured CH_4 or N_2O profiles. To maintain the observed C_2H_6 profile, values of the vertical eddy diffusion coefficient 4 times higher than those used in our 1-D model are required, that is, $K_z = 3 \times 10^4$ cm²/s at 20 km and $K_z = 2 \times 10^5$ cm²/s at 30 km altitude. Such values, however, are rather high for the season and latitude considered [cf. *Climatic Impact Assessment Program*, 1975; *Schmelte-kopf et al.*, 1977] and are not likely to persist for a long time.

Finally, we have to consider horizontal flow. This possibility still requires fast upward transport somewhere, to generate high C_2H_6 concentrations at higher altitudes. Furthermore, the sampling flights were launched during a period of weak easterly flow in the stratosphere over the Eurasian continent which persisted during most of June, as evidenced by the constant pressure charts between 50 and 10 mbar. This leaves little chance for large-scale, horizontal transport fast enough to overcome the fast model-calculated destruction and increase the local C_2H_6 mixing ratios to the observed values. There is, however, some indication that horizontal transport can cause fluctuations in the observed mixing ratios. Many stratospheric profiles of the longer-lived source gases, for example, CH_4, N_2O, and CF_2Cl_2 measured over southern France, and the present ones are no exception, show mixing ratios slightly (about 10%) but systematically increased over the latitudinal average at 25-30 km altitudes. Though less pronounced, the feature is very similar to that observed over 30°N latitude and has been ascribed to meridional transport [*Ehhalt and Tönnissen*, 1979]. On the average, however, this mode of transport seems slow, since H_2 which is produced during the destruction of CH_4 on a time scale of years is also slightly increased. Because it is a relatively slow process and because the fluctuations induced by it on the longer-lived trace gases are small, meridional transport is not likely to cause the large discrepancy observed in the C_2H_6 profile.

There is also a more general argument which places a limit

on any transport-caused deviation from the average C_2H_6 profile. $CFCl_3$ and CF_2Cl_2 reach vertical gradients and chemical lifetimes in the middle stratosphere similar to the ones of C_2H_6 in the lower stratosphere. In fact, at mid-latitudes the measured gradient of $CFCl_3$ approaches the model-calculated one of C_2H_6 already at 20 km altitude. The lifetime of $CFCl_3$ is 1 month at 30 km altitude. Therefore by analogy, C_2H_6 profiles in the lower stratosphere should respond to similar changes in the transport with similar deviations from the average, as do $CFCl_3$ and CF_2Cl_2 in the middle stratosphere. The scatter of the $CFCl_3$ data should provide an estimate for the expected deviations from the average C_2H_6 profile. The observed $CFCl_3$ and CF_2Cl_2 mixing ratios around and above 30 km altitude deviate not more than a factor of 5 from the measured average [*Fabian et al.*, 1979b]. This should represent a reasonable upper limit on the transport-caused deviation from the average C_2H_6 profile. The limit is conservative because it includes the error of the $CFCl_3$ measurement, which becomes quite large for the small concentrations above 30 km altitude. The upper limit of a factor of 5 is much less than the deviation between measured and model-calculated C_2H_6 profiles, which has increased to a factor of 100 at 25 km altitude (cf. Figure 2).

None of the arguments given above is sufficiently strong to exclude transport as being at least partly responsible for the deviation between measured and calculated C_2H_6 profiles. In fact, such deviations are to be expected. However, because the difference between the measured C_2H_6 profile and the one predicted by the 1-D steady state model is so large, it is difficult to blame it all on a peculiar transport pattern. More likely, the model-calculated destruction rate of C_2H_6 is overestimated. Because reaction with OH contributes only 10% of the total destruction above 20 km altitude, that reaction path can be excluded. Apparently, the measured C_2H_6 profile demands a lower Cl concentration than that predicted by our or other present 1-D models, since the reaction rate constant K_1, by *Manning and Kurylo* [1977], used here appears to be essentially correct. Except for an old measurement by *Fettis and Knox* [1964] which gave a rate constant nearly a factor of 2 slower, the published data of *Davis et al.* [1970] and *Baulch et al.* [1980], who cited unpublished data of R. J. Lewis et al. (1980), R. T. Watson et al. (1980), and R. T. Watson and G. Ray (1980), agree with the measurements of *Manning and Kurylo* [1977] to better than 20% for the whole stratospheric temperature range. To explain the observed C_2H_6 profile, the rate constant K_1 would have to be slower by a factor of 4.

Because the measured C_2H_6 profile in Figure 2 may differ considerably from the global average, a definite profile of the Cl atom concentration cannot be derived. To estimate how much the Cl concentration in the lower stratosphere may differ from the model-predicted one, we proceed with the assumptions that the measured C_2H_6 profile represents the global average and that transport can be described by vertical eddy diffusion as in the 1-D model. With that we can estimate the vertical flux divergence of C_2H_6, which in steady state is balanced by the destruction rate of C_2H_6. It is expressed as the inverse of the destruction time, or chemical lifetime, τ_E:

$$\tau_E^{-1} = \frac{1}{\rho M} \cdot \frac{\partial}{\partial z} \left[\rho \cdot K_z \cdot \frac{\partial M}{\partial z} \right] = K_1[Cl] + K_2[OH] \quad (1)$$

where M is the measured C_2H_6 mixing ratio, ρ the number density of air, and K_z the eddy diffusion coefficient used in our

model. The resulting (experimental) τ_E is shown in Figure 4. Since the measured mixing ratio profile fits an exponential decrease with a scale height $h = 3.5 \pm 0.15$ km (see above), the height dependence of τ_E is dominated by that of ρ and K_z; τ_E is often approximated by h^2/K_z, which is also shown in Figure 4. From it the form of our K_z profile can be easily derived. For comparison the model-predicted lifetime of C₂H₆ is also shown in Figure 4. It is given by

$$\tau_c^{-1} = K_1[Cl]_c + K_2[OH]_c = \frac{1}{\rho M_c} \cdot \frac{\partial}{\partial z}\left[\rho \cdot K_z \cdot \frac{\partial M_c}{\partial z}\right] \quad (2)$$

where the quantities to the right are all taken from the model.

The comparison given by Figure 4 shows clearly that τ_E is substantially longer than τ_c above 14 km altitude. In the lower stratosphere the experimental lifetimes of C₂H₆, τ_E, range between 200 and 20 days, which would also tend to decrease the transport-caused deviations from the average C₂H₆ profile. Obviously, the experimentally deduced destruction rate of C₂H₆ by Cl is smaller than that predicted by the model. In order to obtain an estimate for the Cl profile that would explain our C₂H₆ measurements, we use equation (1); τ_E is taken from Figure 4, and K_1 from *Manning and Kurylo* [1977]. Reaction with OH is neglected. Consequently, the Cl concentrations are overestimated, and the derived Cl profile presents rather an upper limit. It is shown in Figure 3 as profile Cl. The Cl concentrations derived from the measured C₂H₆ are considerably lower (up to a factor of 10) than the model-predicted profile. Below 20 km altitude an increasing fraction of C₂H₆ reacts with OH. There the neglect of reaction with OH leads to a considerable overestimate of the Cl concentration, which causes the derived upper limit to curve to higher Cl concentrations. Introduction of the new reaction rate for OH and HNO₃ [*Wine et al.*, 1981] would decrease the model-calculated Cl profile in the lower stratosphere by a factor of 1.5–2 (S. Liu, private communication, 1980). Even so, the derived upper limit remains considerably lower than the model-calculated Cl profile. Clearly, if subsequent measurements give a global C₂H₆ profile similar to the present measurements, a substantial revision of the Cl concentration in the lower stratosphere will be required. The above Cl concentrations are averages over the lifetime of C₂H₆. Because transport within the estimated lifetimes of C₂H₆ (20–200 days) can be extensive, the Cl values should also represent a large-scale horizontal average.

Given the preliminary and limited nature of the C₂H₆ data, much of the foregoing discussion is somewhat tentative. Nevertheless, the present analysis shows for our assumptions and for one particular case that the average Cl concentration in the lower stratosphere is lower than that predicted by current models. It is interesting to note that the ClO measurements by *Anderson et al.* [1977] in the lower stratosphere also give values lower by up to a factor of 5 than the 1-D model calculations. The analysis also shows that extensive stratospheric C₂H₆ measurements of sufficient accuracy are a useful tool for determining the average Cl concentration in the lower stratosphere.

CONCLUSION

It has been shown that the measurement of C₂H₆ can be used to derive profiles of atomic chlorine in the lower stratosphere. This is especially interesting, because the only available technique for measuring Cl directly, resonance fluores-

cence, is restricted to higher altitudes. Even though ClO can be measured to as low as 25 km altitude, the resonance fluorescence technique does not provide measurements of atomic Cl below 35 km altitude [*Anderson et al.*, 1977]. For this reason there is also no altitude overlap with our estimate of Cl from C₂H₆ measurements, and thus a direct comparison with the Cl data by *Anderson et al.* [1977] is not feasible. Because a considerable fraction, about one half, of the O₃ destruction by ClO$_x$ proceeds below 30 km, the implication of lower Cl concentrations at these lower altitudes is important in the estimate of anthropogenic perturbations, and a measurement of the Cl at these lower altitudes is of great interest. If the problem of contamination can be overcome, which seems feasible, the measurement of C₂H₆ by our technique could probably be extended to 35 km and provide data for calculation of an average vertical Cl profile in the lower and middle stratosphere.

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