SHORTER CONTRIBUTION

Decrease of carbon monoxide mixing ratio above the polar tropopause

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It is now established that CO is a regular constituent of the troposphere with mixing ratios ranging from about 0.1 to 0.2 ppm in uncontaminated air (see e.g. the compilation of newest data by Robinson & Robbins, 1967). Bates & Witherspoon (1952) estimated that the only major source of CO is automobil exhaust and this conclusion is still valid except perhaps for layers of high CO concentration in ocean waters recently detected by J. W. Swinnerton *et al.* (1968). The best estimates of world wide CO production and tropospheric content result in tropospheric life times of about 3 years which is short compared with other gaseous constituents in the atmosphere but rather long for a pollutant. Next to the world wide increase in CO_2, CO is the major global air pollutant and is therefore of particular interest to air chemistry.

A special problem is the fact that at the present time we do not know of any efficient process of removal of CO from the atmosphere. The ocean cannot act as an important sink of CO due to the low solubility of 0.02 cm^3 CO/gH_2O at normal temperature and due to the occurrence in ocean water of concentrations higher than equilibrium. An interesting possibility is removal by oxidation. The reaction with O_2 is much too slow to be of any importance in the atmosphere (Bates & Witherspoon, 1952). Above the tropopause among others the constituents O_3, H_2O_2, HO_2, $O(^3P)$ are or should be present in the order of their concentration (Hesstvedt, 1968) and may react with CO to form CO_2. The rates given by Leighton (1961) for the reaction $CO + O + M \rightarrow CO_2 + M$ are again too slow. The same can be expected for O_3 although the experimental evidence is uncertain for atmospheric conditions (Garvin, 1954; Leighton, 1961) For H_2O_2, HO_2 nothing is known. Dissociation of carbon monoxide can be excluded as a sink in the stratosphere because the high energy of dissociation near 1300 Å is only available at much higher levels. Bates & Witherspoon (1952) concluded that the stratosphere does not represent a sink area of importance. On the basis of the incomplete information on possible reactions and reaction rates, this conclusion must be regarded tentative.

One way to test these possibilities is by measuring the vertical distribution of CO up to stratospheric levels. On the basis of a recently developed method for determining small concentrations of CO in air by Robbins *et al.* (1968), an instrument was built (Seiler & Junge, 1967) capable of recording continously the CO content on board an aircraft with the necessary sensitivity and reliability, details of which will be given elsewhere. The limit of detection was about 3 ppb, the calibration linear with periodic checks on board. In cooperation with the Lufthansa we arranged for measurements on board a commercial aircraft using the cabin ventilation system. The air in this system reaches the outlets in the cabin within a few seconds after intake by the compressor. The high flow capacity and the separation of this system from the aircraft engines minimize any possible contamination. Unfortunately, it is not possible to check this during flights and it is also impractical to do so on an aircraft grounded at the airport due to the fluctuating level of CO on a busy airport. The results of the flights, however, strongly suggest that the ventilation system indeed supplies rather representative outside air.

Several transpolar flights on the route Frankfurt–Anchorage–Tokyo were made primarily in

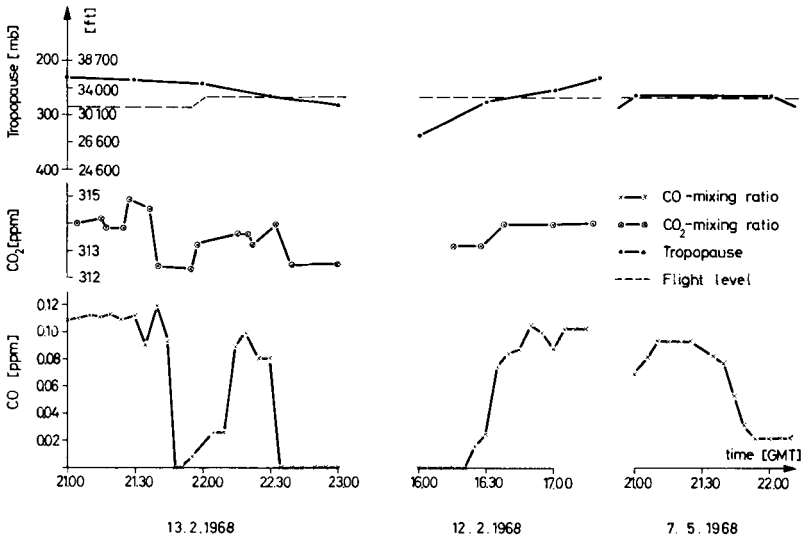

Fig. 1. Three examples of CO and CO_2 mixing ratios during crossings of the tropopause.

order to penetrate into the stratosphere as far as possible. We obtained data during the following days: 31.1.–1.2.68; 12–13.2.68; 24–25.4.68; 7–8.5.68.

The flight level was such that on all flights sections within the troposphere alternated with those within the stratosphere. The CO mixing ratio in the troposphere fluctuated between about 0.1 and 0.2 ppm with values around 0.1 ppm below the tropopause in agreement with measurements in clean surface air. In the stratosphere the values rapidly dropped below 0.03 ppm and often reached the detection limit. The decrease or increase of mixing ratio usually occured within a few minutes of crossing the tropopause. Fig. 1 gives a few examples.

Unfortunately, it is difficult for transpolar flights to determine the location of the aircraft with respect to the tropopause with the desired accuracy due to the small number of radiosonde stations along this route. Some help was provided by inflight measurements of temperature by the crew and observations of turbulence. Further information was supplied by simultaneous records of CO_2 which show a small but distinct difference in concentration between stratosphere and troposphere due to the seasonal variation of CO_2 within the troposphere which does not penetrate far into the stratosphere. The CO_2 recordings were obtained by the Meteorological Institute of the University of Frankfurt and kindly supplied to us for evaluation. The CO_2 recorder was also attached to the cabin ventilation system. Despite this observational support it was not always possible to correlate the chemical and the meteorological data for tropopause crossings exactly. Besides this difficulty it should be considered that the technically defined tropopause may not always be identical with the true thermal tropopause and that the thermal tropopause may not be identical with the chemical tropopause as e.g. demonstrated by the numerous ozone recordings of the North America network (Hering and Borden, 1967). The experience during the flights demonstrated, however, that the CO level was a good indicator for the tropopause. Unfortunately, it was not possible to make ozone recordings during these flights.

Careful laboratory tests showed that the presence of ozone in air at stratospheric concentration levels had no effect on the indication of the CO-meter. This eliminates the possibility that the increase of O_3 above the tropopause may have caused the drop of CO by interference within the instrument. Although the aircraft was never more than about 3 km above the tropopause during these flights the data give strong evidence that quite generally the tropospheric CO mixing ratio drops rapidly to very low levels within the stratosphere. Estimates using such vertical gradients and eddy diffusion

coefficients of 5×10^3 cm²/sec indicate that the resulting fluxes of CO into the stratosphere are of the right order to explain the tropospheric life time of a few years. If this can be confirmed destruction above the tropopause may be considered the major sink for atmospheric CO. The vertical profiles strongly suggest that the decrease in CO mixing ratio must be due to constituents which originate in the stratosphere and have a sink in the troposphere thus resulting in a sharp decrease in concentration below the tropopause (as e.g. ozone). With the information available on reaction rates and stratospheric composition it is not possible to draw further conclusions at the present time.

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