

HO_x, NO_x, and ClO_x: Their Role in Atmospheric Photochemistry

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Received November 26, 1973

Sources of atmospheric odd nitrogen and hydrogen are reviewed and their role in ozone photochemistry is discussed. A model, containing few adjustable parameters, gives good agreement with observed distributions of stratospheric and mesospheric ozone. Nitric oxide emitted by supersonic aircraft would lead to a significant reduction in the concentration of atmospheric ozone if the globally averaged source of NO should exceed 2×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$. A traffic model projected by Broderick *et al.* for 1990 could lead to a reduction of about 2% in the column density of O₃.

Sources of atmospheric chlorine are discussed. It is argued that HCl should be the dominant form of atmospheric chlorine and that it is produced mainly from aerosols of marine origin. The atmospheric source strength is about 2×10^7 tons per year according to Chesselet *et al.* and HCl may be removed by gas phase reaction with NH₃. The role of chlorine compounds as a catalyst for recombination of odd oxygen is discussed and shown to play no major role in the normal atmosphere. Reactions of OH and HO₂ with O₃ may provide an important sink for tropospheric odd oxygen such that O₃ may not be a passive tracer for tropospheric motions.

Les sources de quelque azote et hydrogène atmosphériques sont revues et leur rôle dans la photochimie de l'ozone est étudié. Un modèle, contenant deux paramètres ajustables, est en bon accord avec les distributions d'azote stratosphérique et mésosphérique observées. L'oxyde nitrique émis par des avions supersoniques amènera une réduction significative de la concentration de l'ozone atmosphérique si la moyenne globale de la source de NO doit dépasser 2×10^7 molécules $\text{cm}^{-2} \text{s}^{-1}$. Un modèle de trafic, projet de Broderick *et al.*, pour 1990 pourra mener à une réduction de près de 2% dans la densité de la colonne d'O₃.

Les sources du chlore atmosphérique sont étudiées. On démontre que HCl est la forme dominante du chlore atmosphérique et qu'il est produit essentiellement d'aérosols d'origine marine. D'après Chesselet *et al.*, la force de la source atmosphérique est de près de 2×10^7 tonnes par an, et le HCl peut être éliminé par une réaction en phase gazeuse avec NH₃. Le rôle des composés du chlore comme catalyseur pour la recombinaison de quelque oxygène est étudié et démontre jouer aucun rôle majeur dans l'atmosphère normale. Les réactions du OH et du H₂O avec du O₃ peuvent fournir un important affaiblissement pour quelque oxygène troposphérique tel que O₃ ne pourra être un traceur passif pour les déplacements troposphériques. [Traduit par le journal]

Can. J. Chem., 52, 1582 (1974)

Introduction

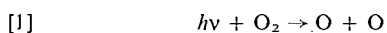
The intent here is to provide a brief summary of recent work on the transport and chemistry of trace stratospheric gases which are now believed to play a role in determining the equilibrium concentration of atmospheric ozone. The summary is in no sense complete, neither in content nor in reference to original material. More general reviews are given elsewhere in this volume by Crutzen (1) and Nicolet (2). We shall emphasize simple one-dimensional model studies carried out in this laboratory and particularly highlight models which relate to the possible perturbation of the stratosphere by future fleets of supersonic aircraft. We shall offer a brief discussion of chemical processes as they affect the distribution of

chlorine compounds in the atmosphere. The work on chlorine had as its impetus the possible modification of the stratosphere by the space shuttle. The shuttle, now under development and scheduled for operation in the 1980's, will emit HCl as an exhaust product. A systematic study of its consequences is now in progress under the auspices of the National Aeronautics and Space Administration. This paper offers an initial attempt to define the problem and an attempt to focus on some of the major uncertainties and targets for future research.

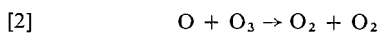
Ozone in the Normal Stratosphere

Odd oxygen atoms are produced in the atmosphere mainly by dissociation of O₂ in the

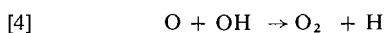
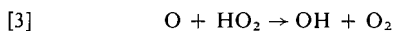
Herzberg continuum:



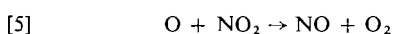
They are removed in the stratosphere by the simple reaction



first discussed by Chapman (3), and by more complex reaction schemes terminating in

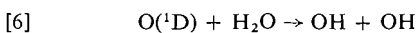


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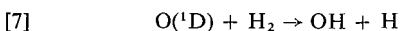


The importance of HO_x, in the context of the ozone problem, was first recognized by Bates and Nicolet (4). The importance of NO_x was identified by Crutzen (5). For present purposes we define HO_x as H + OH + HO₂, NO_x as N + NO + NO₂ + NO₃ + 2·N₂O₅ + HNO₂ + HNO₃.

The major source of stratospheric HO_x is the reaction



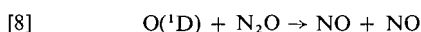
with a small contribution from



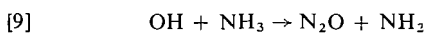
and a similar reaction with methane.

NO_x is formed by oxidation of N₂O and NH₃, and by dissociation of N₂ following absorption of cosmic rays.

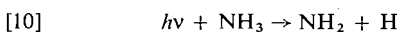
The primary oxidation process for N₂O is



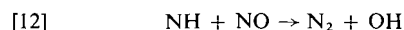
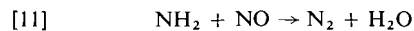
and this source of stratospheric NO_x has been relatively well characterized in the recent literature (6-8). The contribution from NH₃ remains somewhat uncertain. Stratospheric ammonia is believed to be removed mainly by reactions such as



and



The subsequent details of the reaction scheme are uncertain. It is reasonable to expect NO and NO₂ as major products. One cannot, however, rule out the possibility that [9] and [10] might lead to a net sink for stratospheric NO_x through reactions such as

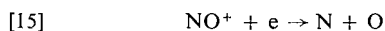
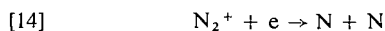


as discussed by McConnell (9) and McConnell and McElroy (10). Further laboratory data are required to clarify the situation. In addition, there is an urgent need for atmospheric measurements of NH₃ and its possible products. Later in this paper we shall argue that formation of aerosols would provide a major sink for atmospheric NH₃. Aerosol formation could be initiated by a gas phase reaction of NH₃ with HCl

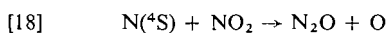
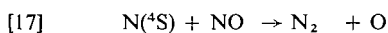


or a similar reaction with HNO₃. If further work confirms this possibility, it may be necessary to extend present chemical models for the stratosphere to include reactions involving chlorine compounds, notably HCl, ClO, Cl₂, Cl, and NH₄Cl. In the meantime, the contribution of NH₃ chemistry to the stratospheric NO_x budget remains uncertain.

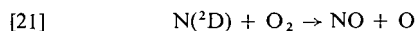
Absorption of cosmic rays initiates a complex chemistry (11) in which NO_x is formed by reactions such as



The product atoms may be released in excited states and it is especially important to define the relative yields of N(⁴S) and N(²D). Excess production of the former can lead to net destruction of NO_x by reactions such as



The latter will be efficiently quenched in the stratosphere with production of NO by the reaction



Reaction 21 is the major source of NO in the atmosphere above 100 km, while [17] is the dominant sink for mesospheric and thermospheric odd nitrogen.

The potential importance of the cosmic ray related source of stratospheric NO_x has been emphasized in a recent paper by Ruderman and

Chamberlain (12). They pointed out that the cosmic ray flux reaching the atmosphere is largest at times of low solar activity and that its effects are confined mostly to high geomagnetic latitudes. NO_x produced at high latitudes must be transported to low latitudes before it can have any significant effect on O_3 . Subsequent modification of O_3 should be phase shifted with respect to the cosmic ray source, and Ruderman and Chamberlain (12) made some preliminary estimates of the magnitude of the phase shift. Their estimates are in satisfactory agreement with phase shifts observed by Angell and Korshover (13) in an analysis of ozone data taken at Tromso and Arosa (see also ref. 14). The importance of Ruderman and Chamberlain's contribution is twofold. First, it provides a reasonable mechanism to account for the much discussed correlation not heretofore widely accepted by the meteorological community. Second, the work implies that absorption of cosmic rays in the stratosphere may indeed lead to significant production of NO_x which should be included in detailed attempts to model stratospheric chemistry and dynamics. A major uncertainty is the estimation of the rate of NO_x production by cosmic rays, for which experimental data are lacking.

Estimates for the concentration of major forms of NO_x and HO_x are given in Figs. 1 and 2. The results shown here were taken from the study by McElroy *et al.* (15) and are intended to represent mean (24 h average) conditions at a latitude of 30°N , for a solar declination of $+12^\circ$. The tropopause is at 16 km. In the context of O_3 photochemistry we are particularly concerned with concentrations of NO and NO_2 for the height

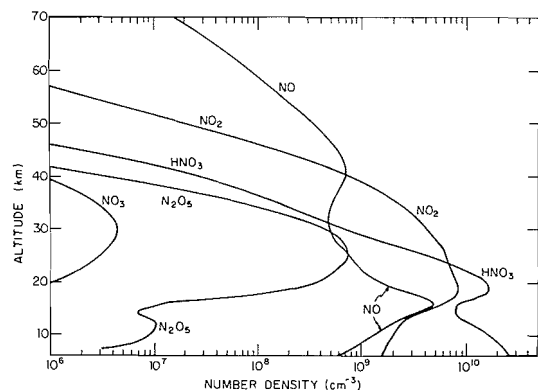


FIG. 1. Calculated vertical distributions of individual NO_x constituents in the normal atmosphere, 30°N latitude, solar declination $+12^\circ$. From McElroy *et al.* (15).

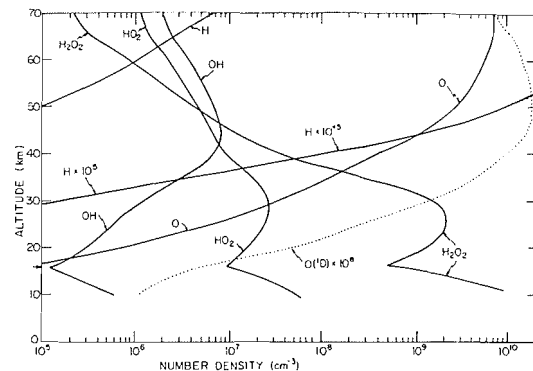


FIG. 2. Calculated number densities (24 h average) for hydrogenous radicals, H_2O_2 , $\text{O}(^3\text{P})$, and $\text{O}(^1\text{D})$ for the normal atmosphere, 30°N latitude, solar declination $+12^\circ$. The tropopause is at 16 km. From McElroy *et al.* (15).

range 30 to 50 km, and with concentrations of H and OH above 50 km. The concentration of O_3 below 30 km is controlled mainly by dynamics. Reaction 5 is the major loss process for odd oxygen below 45 km. The Chapman reaction 2 is important between 45 and 55 km, whereas reactions 3 and 4 dominate above 55 km.

The concentration of NO_x in the important height range 30 to 50 km is determined by a balance of input associated with oxidation of N_2O , reaction 8, and removal by vertical transport. Analyses of the various uncertainties are given by McConnell and McElroy (10) and by McElroy *et al.* (15). They concluded that the concentration of NO_x should be relatively well determined for this height range, although major uncertainties may remain at lower elevations. Vertical motion was treated using the expedient concept of eddy diffusion, with diffusivities chosen to reproduce observed concentrations of CH_4 and N_2O (16).

McElroy *et al.* (15) used the concentrations of NO_x and HO_x given in Figs. 1 and 2 to compute concentrations of O_3 . The calculation is relatively straightforward for the atmosphere above 30 km where photochemical processes dominate for odd oxygen. Results are shown in Fig. 3, which includes also a comparison with observational data obtained by Johnson *et al.* (17), Hering and Borden (18), Hilsenrath *et al.* (19), and Krueger *et al.* (20). Theory agrees with experiment within permissible observational error limits. The agreement is taken as a measure of the overall validity of the techniques employed to calculate NO_x and

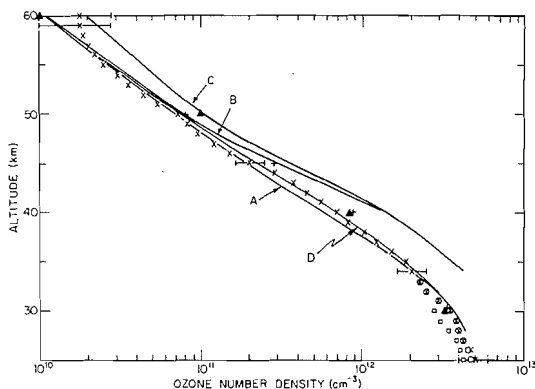


Fig. 3. Calculated ozone profiles are shown for the normal atmosphere, 30° N latitude, +12° solar declination. Curve A was calculated with the complete chemical model and computed NO_x profiles; reactions involving NO_x were omitted in curve B; reactions involving NO_x and HO_x were omitted in curve C. Curve D was the same model as A, but with a slower value for the reaction rate of NO with O₃ (cf. ref. 15). Observations shown are as follows: Hilsenrath *et al.* (19), X, (with error bars) chemiluminescent rocketsonde, and O, Mast-Brewer electrochemical balloonsonde, at Wallops Is. (38° N), Sept. 16, 1968; Δ, Johnson *et al.* (17), as corrected by Evans *et al.*, rocketsonde solar u.v. absorption from White Sands (32° N), June 14, 1949; +, Krueger *et al.* (20), rocketsonde solar u.v. absorption from Pt. Magu, Calif. (34° N), June 18, 1970; □, Hering and Borden, Mast-Brewer balloonsondes from Tallahassee, Fla. (30.4° N), 1966 summer average. Figure taken from McElroy *et al.* (15).

HO_x and lends support to the general reliability of the theoretical model.

Modification of Ozone by Supersonic Aircraft

We shall model possible effects of NO_x introduced into the stratosphere by high flying aircraft. We consider aircraft at cruise altitudes of 17, 20, and 25 km. The lowest altitude is appropriate for the Concorde. The intermediate value is adopted for an advanced version of the American supersonic transport (SST), and the highest value could apply for a conceptual future hypersonic transport (HST). We shall model the vertical distribution of NO_x input for a given aircraft with a triangular shape function centered on the appropriate altitude. The triangular function is taken to give a vertical extent of 2 km at the half-intensity point for the Concorde and HST. A somewhat broader width of 4 km is adopted for the SST.

Emission rates of NO_x are of course largely unknown for SST and HST. We adopted data given by Broderick *et al.* (21) for the Concorde.

From their emission rates we estimate that Concorde, carrying 100 passengers at a cruise speed of 2.1×10^3 km h⁻¹ for approximately 7 h per day, would emit a globally averaged quantity of NO_x equivalent to 7.74×10^4 molecules cm⁻² s⁻¹. Similarly, the corresponding NO_x emission rate for SST would be 5.73×10^5 molecules cm⁻² s⁻¹, with an assumption that the advanced SST should carry 600 passengers at a cruise speed of 3.2×10^3 km h⁻¹, for 7 h a day.

A summary of the various computations for O₃ in the perturbed atmosphere is given in Fig. 4. An effort was made in these computations to include all of the possible feedback mechanisms which occur in the perturbed atmosphere. For example, a perturbation of ozone leads to a change in the transmission of the atmosphere at ultraviolet wavelengths, with a resulting alteration in the source of odd oxygen. A change in atmospheric transmission also affects the natural source of NO_x associated with reactions 8 through 10. Reduction in the concentration of O₃ leads to a decrease in computed values for stratospheric temperature with consequent effect on the rates of various chemical reactions. These feedback mechanisms were properly included in all computations for the perturbed environment. The consequence of thermal adjustment is shown explicitly in the figure.

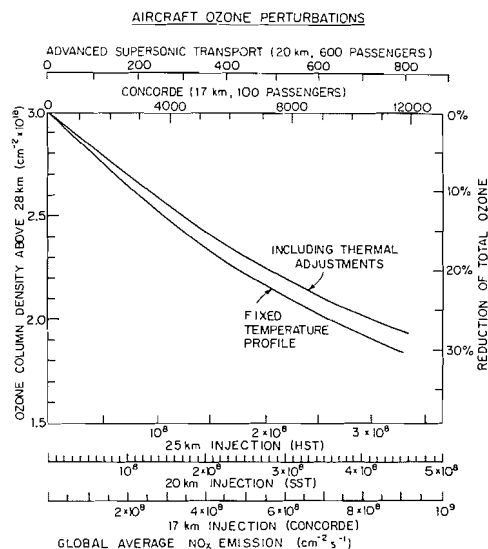


Fig. 4. Perturbations in ozone induced by artificial injections of NO_x. A detailed discussion of the various scales is given in the text. Figure taken from McElroy *et al.* (15).

The left vertical axis in Fig. 4 gives the column density computed for O_3 in the atmosphere above 28 km, at a latitude of $30^\circ N$ for a solar declination of 12° . Results are shown for a variety of NO_x inputs as given by the separate scales for the bottom horizontal axis. We note that the perturbation in ozone expected for a given input of NO_x is a moderately sensitive function of the height at which injection occurs. For example, an input of NO_x equivalent to 2×10^8 molecules $cm^{-2} s^{-1}$ at 25 km leads to a reduction by approximately 25% in the computed column density of O_3 above 28 km. The inputs required at 20 and 17 km in order to provide a similar reduction in O_3 are 2.75×10^8 and 5.5×10^8 $cm^{-2} s^{-1}$ respectively. A fleet of 775 Concordes flying for 7 h a day at 17 km would reduce O_3 above 28 km by 3%. A traffic model projected by Broderick *et al.* (21) for 1990 would provide for a corresponding reduction of 2.4% for O_3 above 28 km.¹

The right vertical axis in Fig. 4 shows an attempt to define the approximate change in total O_3 column due to aircraft operations. For present purposes we assume that the atmosphere consists of two distinct regions. In one zone chemical time constants for O_3 are short compared with time constants for dynamics, and the concentration of O_3 should be accurately modeled by a photochemical equilibrium theory. In the second zone, dynamical time constants are short compared with chemical values, and the distribution of O_3 is set by the details of the atmospheric motion field. The boundary between these two zones describes a surface whose height should be an increasing function of increasing latitude. Ozone is released into the dynamical zone primarily at lower latitudes. A reduction in O_3 at the boundary between the chemical and dynamical zones would lead to a reduction in O_3 at all locations within the dynamical zone. The reduction factor will be approximately equal to the reduction which applies in the low latitude region of the boundary surface.

¹The projected 1990 fleet would support an annual traffic volume of 5.9×10^{12} passenger km if aircraft were assumed to fly at all times with a full complement of passengers. This figure may be compared with the present traffic of 4.4×10^{11} passenger km per year. It is assumed that the bulk of air transport in 1990 will be carried by current or improved versions of existing aircraft such as B747 and DC 10. The estimated NO_x emission rate adopted here for the 1990 fleet is 4.3×10^7 molecules $cm^{-2} s^{-1}$ and it is distributed over the height range 16–21 km.

Somewhat arbitrarily, we identify the boundary surface with the level at which the chemical time constant for O_3 is 15 days. Concentrations of O_3 along the boundary can then be derived with the photochemical model and concentrations below the boundary may be scaled accordingly. The reduction factors indicated on the right hand vertical scale reflect this procedure. We believe that the procedures followed here are unlikely to lead to major error. In particular, our conclusions are relatively insensitive to the precise criterion used to define the boundary between the chemical and dynamical zones.²

Origin and Chemistry of Atmospheric Chlorine

There is little doubt that the atmosphere, at least in marine environments, contains significant quantities of gaseous chlorine. The gas was first identified by Junge (22) and was subsequently observed by Duce (23), Buat-Menard and Chesselet (24), and Chesselet *et al.* (25). In all cases, combinations of molecular sieves and filters were used to eliminate particles with radii greater than 0.1μ . In addition, Junge measured the concentration of Aitken nuclei and showed that at most 2% of the transmitted chlorine could be present in these particles. The mixing ratio (v/v) of total gaseous chlorine,³ at least for the marine atmosphere near ground level, is apparently in the range $1-6 \times 10^{-9}$. Junge (22) measured gaseous chlorine just above the trade-wind inversion at Hawaii and found concentrations which were approximately a factor of 2 less than values measured in the near surface area. Chesselet *et al.* (25) observed a decrease in the concentration of gaseous chlorine carried by an air mass of marine origin as the air mass passed over land in rural France. The French data may be interpreted to yield a lifetime for gaseous chlorine in the near surface atmosphere of about 0.4 days, but probably reflects dilution of marine air by chlorine-poor air from aloft.

The studies by Chesselet and associates (24–26) strongly support the hypothesis of a marine ori-

²The analysis given here is not sufficiently precise to allow a quantitative estimate for O_3 reduction at any particular latitude. The estimates in Fig. 4 should be useful at all latitudes. The reduction factor at high latitudes may be somewhat smaller than given here. The reduction at equatorial latitudes could be a little larger than the mean estimates derived in the present analysis.

³We assume here, as justified below, that HCl is the major form of gaseous atmospheric chlorine.

gin for gaseous atmospheric chlorine. Under quiet wind conditions the mixing ratio of gaseous chlorine in marine air is relatively constant with a value between 1.2 and 2.4×10^{-9} . Strong variations in the gaseous mixing ratio were observed as the surface wind speed increased above about 20 knots. The increase in gas phase chlorine was accompanied by a slight decrease in the Cl:Na observed in the particulate phase, and Chesselet *et al.* (25) estimated that approximately 3% of the chlorine initially present in the particulate phase was eventually released as gas. This figure implies a net global production of gaseous chlorine equal to about 2×10^8 tons per year when combined with the estimate (25) of 6×10^9 tons per year for the total quantity of particulate chlorine injected into the atmosphere, mainly by bubbling at the sea surface (27). This production may be compared with the source from volcanoes estimated to be approximately 9×10^6 tons per year (28). Gaseous chlorine production associated with industrial activity, mainly HCl, can be estimated in various ways to give approximately 10^7 tons per year, a source strength comparable to the volcanic mechanism but small compared with marine aerosols.

Earlier objections by Valach (29) to the hypothesis of marine origin were effectively answered by Duce (23). Valach argued that the observed deficit of chlorine in the particulate form was not sufficient to account for the rather large concentrations of gaseous chlorine observed. The apparent contradiction is readily resolved. The lifetime for the gaseous component is much longer than that for the particulate form. Thus even a small efficiency, 3%, for the conversion from particle to gas is sufficient to account for comparable abundances of chlorine in the separate phases of the atmosphere. This matter is discussed further by Buat-Menard (26), Buat-Menard and Chesselet (24), and Chesselet *et al.* (25).

Mechanisms for production of gaseous chlorine from marine particles are discussed by Robbins *et al.* (30) and by Eriksson (28). Robbins *et al.* believed that atmospheric NO₂ could be hydrolyzed in the vapor phase to form HNO₃, with the latter dissolving in sea salt particles, lowering the pH of the particles, and subsequently releasing HCl. Eriksson also favored HCl as the gaseous product but thought that SO₃ was a more likely candidate than HNO₃ as the absorbed species responsible for the necessary

reduction in the pH of the particles. The precise mechanism remains unclear. Laboratory studies by Buat-Menard (26) leave little doubt, however, that gaseous chlorine is indeed produced when marine particles are exposed to common atmospheric air. Gaseous chlorine was not observed if procedures were implemented to eliminate gases such as SO₃ and H₂SO₄ in the air stream to which the particle sample was exposed.

If we adopt a mean value of 1.2×10^{-9} for the mixing ratio of gaseous atmospheric HCl, consistent with the preceding discussion, we can readily compute a mean value for the corresponding atmospheric lifetime. If we consider a net global HCl source of 2.2×10^8 tons per year, we estimate a mean lifetime of 9.5 days,⁴ which may be compared with the empirical lifetime of 0.4 day derived by Chesselet *et al.* (25) over rural France. The two results can be reconciled if we assume that the major sink for HCl occurs over land and if we assume that only 15% of the land mass is effective as a sink for HCl. This figure might be reasonable if the sink involved a spatially variable minor component of the atmosphere. Ammonia could be a suitable candidate and reaction 13 might provide a plausible mechanism. Measurements by Junge (22), Georgii (31), and Breeding *et al.* (32) indicate that the concentration of NH₃ is indeed variable and suggest that the concentration over land may be significantly higher than marine values. Establishment by Kaplan (33) of a low upper limit (<0.08 p.p.b.) for NH₃ above Mont-Louis is consistent with the similar upper limit on HCl (<0.1 p.p.b.) near the tropopause determined by Farmer (34). Both constituents must have quite short lifetimes (~1 day) if the concentrations are to fall off so dramatically away from the near surface environment. Further work is required in order to elucidate the chlorine removal process. In particular we need data on the global distribution of HCl and NH₃, as well as measurements to define the efficiency of various soils as sinks for HCl. We may note, however, that the effective rate constant for reaction 13 need not be very large, 10^{-35} cm⁶ s⁻¹ would suffice, to account for the observed HCl loss; Mohnen has suggested that NH₄Cl aerosol formation is catalyzed by small ions and has ap-

⁴This lifetime presumes a scale height of 7 km for gaseous atmospheric chlorine. Junge's (22) Hawaiian data suggest that the actual scale height may be somewhat less, perhaps 3 km, and the derived lifetime should be lowered accordingly.

TABLE 1. Chlorine reactions^a

Reaction No.	Rate expression	References and remarks	Reaction
1	$2.1 \times 10^{-11} \exp(-1037/T)$	Takas and Glass (63)	$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$
2	$2 \times 10^{-11} \exp(-2164/T)$	Galante and Gislason (53) Westenberg and deHaas (64) Benson <i>et al.</i> (47)	$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$
3	$1 \times 10^{-11} \exp(-1605/T)$		$\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$
4	$1.88 \times 10^{-11} \exp(-3573/T)$		Wong and Belles (66)
5	1.84×10^{-11}	Clyne and Watson ^c	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
6	$1.6 \times 10^{-33} \exp(800/T)$	Widman and DeGraff (65) Hippler and Troe (55)	$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$
7	1.7×10^{-33}	Johnston <i>et al.</i> (37) Nicholas and Norrish (58)	$\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$
8	$1.3 \times 10^{-11} \exp(-1000/T)$	Clyne and White (49) Johnston <i>et al.</i> (37)	$\text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$
9	$1.3 \times 10^{-12} \exp(-1150/T)$	Johnston <i>et al.</i> (37) Clyne and White (49) Clyne and Coxon (41)	$\text{ClO} + \text{ClO} \rightarrow \text{ClOO} + \text{Cl}$
10	1.44×10^{-12}	Johnston <i>et al.</i> (37)	$\text{Cl} + \text{ClOO} \rightarrow \text{ClO} + \text{ClO}$
11	1.5×10^{-10}	Johnston <i>et al.</i> (37)	$\text{Cl} + \text{ClOO} \rightarrow \text{Cl}_2 + \text{O}_2$
12	1.7×10^{-11}	Clyne and Watson ^c	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$
14 ^b	2.2×10^{-3} 6.0×10^{-5} 2.4×10^{-6} 1.5×10^{-6}	Durie and Ramsay (39) Pannetier and Gaydon (38) Porter (40) Johnston <i>et al.</i> (37) Clyne and Coxon (41)	$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}$
15 ^b	$2.0 \times 10^{-7}, 1.9 \times 10^{-8}, 0., 0.$	Romand and Vodar (60) Myer and Samson (57)	$\text{HCl} + h\nu \rightarrow \text{H} + \text{Cl}$
16	5.3×10^{-11}	Bemand, Clyne, and Watson (42)	$\text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2$
17 ^b	$1.6 \times 10^{-3}, 1.4 \times 10^{-3}$ $1.3 \times 10^{-3}, 1.3 \times 10^{-3}$	Gibson and Bayliss (54) Seery and Britton (61)	$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$
22	5×10^{-32}	Johnston <i>et al.</i> (37) Net reaction	$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2 + \text{O}_2 + \text{M}$
23 ^b	$1.9 \times 10^{-3}, 9.8 \times 10^{-8}, 0., 0.$	Johnston <i>et al.</i> (37)	$\text{ClOO} + h\nu \rightarrow \text{Cl} + \text{O}_2$
27	3.5×10^{-11}	Stedman <i>et al.</i> (62)	$\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$
28	$1.36 \times 10^{-11} \exp(-1560/T)$	Niki and Weinstock (59) Clyne and Coxon (48)	$\text{O} + \text{Cl}_2 \rightarrow \text{ClO} + \text{Cl}$
30	0.	Assumed	$\text{ClO} + \text{O}_3 \rightarrow \text{ClOO} + \text{O}_2$
32	1×10^{-11}	Estimate	$\text{H} + \text{ClO} \rightarrow \text{HCl} + \text{O}$
34	1×10^{-11}	Estimate	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$
35	0.	Assumed	$\text{ClOO} + \text{O}_3 \rightarrow \text{ClO} + 2\text{O}_2$
37	$5 \times 10^{-11} \exp(-1791/T)$	Clyne and Walker (50) Davis, Braun, and Bass (52)	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$

^aAll concentrations are assumed in units of cm^{-3} .

^bPhotolysis rates are 24 h means and are given at 50, 30, 15, and 0 km altitudes.

^cPreliminary results communicated by R. T. Watson.

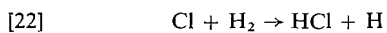
parently observed particle formation (see ref. 35). The NH_4Cl mechanism is consistent with Junge's (22) Hawaiian observations carried out at an elevation of 3 km. He found that the gaseous precursors of NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} at 3 km were all reduced relative to their ground level values in proportions consistent with removal of NH_4Cl , NH_4NO_3 , and $(\text{NH}_4)_2\text{SO}_4$.

It has been well known since the early work of Norrish and Neville (36) that gaseous chlorine can photosensitize recombination of O_3 . A vari-

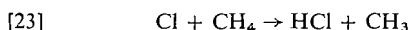
ety of reactions has been studied more recently and many of the important rate constants have been measured (see for example ref. 37). Chlorine compounds are also known to react with other important minor constituents of the atmosphere, such as CH_4 , H_2 , NO , and possibly N_2O . A summary of the various important reactions and rate constants is given in Table 1. In order to investigate their possible effect on atmospheric O_3 , we consider a situation in which the mixing ratio of total chlorine has the value 10^{-9} , at all

altitudes. The consequent distribution of major chlorine compounds is shown in Fig. 5.

The major components are HCl and ClO, at least with the particular reaction scheme adopted here. The important source reactions for HCl are



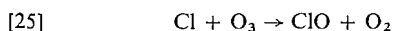
and



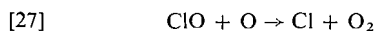
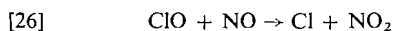
The gas is removed by



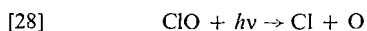
Reaction of Cl with O₃ provides the dominant source of ClO:



The major sinks are



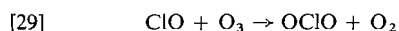
and



with [26] playing a major role in the troposphere and lower stratosphere. The rate for photolysis of ClO is not well known. The weak near u.v. absorption bands (4,0), (3,0), ..., (0,0) were not included in the present analysis since the upper levels were apparently observed in emission by Pannetier and Gaydon (38) and there is no evidence for predissociation (see also ref. 39). We extrapolated data by Johnston *et al.* (37) and Porter (40) in order to estimate the contribution of longer wavelengths to the net photolysis rate. Despite these uncertainties, the results shown in Fig. 5 should be reasonably reliable. Photolysis

of ClO makes only a minor contribution (<10%) to the major chemical paths in the present model.

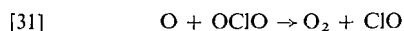
We omitted possible formation of OCIO by the reaction



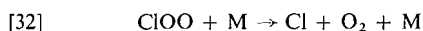
The reaction is surely slow (*cf.* ref. 41) and would be followed by photolysis



although there might be some net loss of odd oxygen by the relatively slow reaction (42)



The dominant chlorine removal of odd oxygen, however, is provided by [27], and reactions involving ClOO and OCIO most likely make no more than a small contribution to the total O removal rate. The radical ClOO is removed mainly by



with a small contribution due to photolysis



The possible effects of chlorine catalysis on atmospheric O₃ are summarized in Fig. 6. The results given here were obtained following the procedures described by McElroy *et al.* (15), modified to include the chlorine reactions in Table 1. Strengths of various loss processes for odd oxygen are shown in Fig. 7 for an assumed mixing ratio of 10⁻⁹. Although effects of chlorine catalysis extend over a wide height range, their

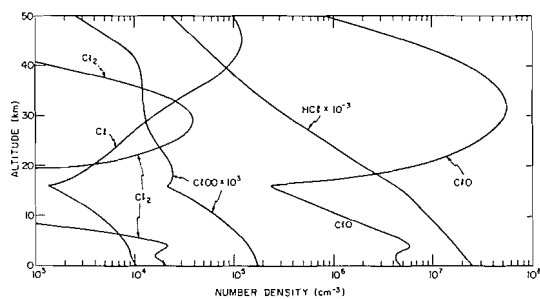


FIG. 5. The distribution of gaseous chlorine constituents is shown as a function of altitude in the troposphere and stratosphere. The total mixing ratio of all gaseous chlorine compounds has been arbitrarily set at $f = 1 \times 10^{-9}$ (v/v).

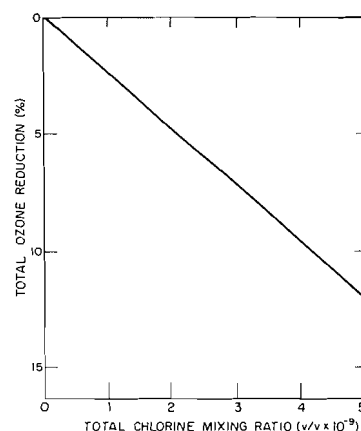


FIG. 6. Catalytic reduction of ozone is shown as a function of the mixing ratio for all forms of gaseous chlorine. The ozone reduction was calculated by the method of McElroy *et al.* (15).

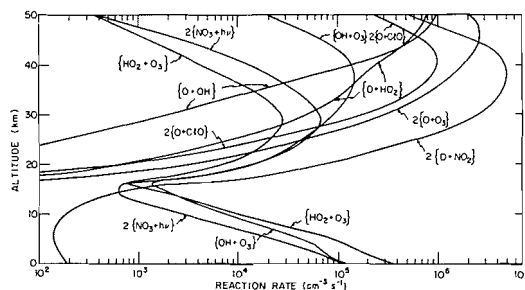


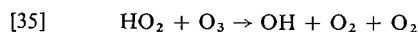
FIG. 7. Recombination of O and O₃ is shown in terms of the elementary reaction rates. The mixing ratio of total gaseous chlorine has been arbitrarily chosen as $f = 1 \times 10^{-9}$ (v/v).

influence is generally small compared with reactions 3 through 5. If one accepts Farmer's (34) upper limit for the mixing ratio of stratospheric HCl, 10^{-10} , and the results in Fig. 5 which indicate that HCl is the major chlorine compound, it would seem to follow that chlorine catalysis can at most play a minor role in the normal atmosphere. It should be emphasized, however, that the various sinks for HCl discussed here (reaction with NH₃, rain out, wash out, heterogeneous absorption) are effective only at low altitudes, below about 18 km. The space shuttle would provide a source of HCl which would extend to high altitudes, ~50 km, where natural sources of HCl are either very small or totally absent. The effects of such high altitude sources merit further study but cannot be reliably assessed until such time as the natural chlorine cycle is better established. We may note that the space shuttle could affect the stratospheric NO_x budget by increasing the effective loss rate of NH₃ through [13]. Reactions involving N₂O, for example

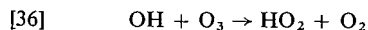


are also possible though not established. Finally we note that chlorine from the shuttle could have an indirect influence if reactions such as 22 and 23 could provide a source of HO_x comparable to reactions 6 and 7 which control HO_x production in the normal atmosphere.

We may note in Fig. 7 the apparent importance of reactions

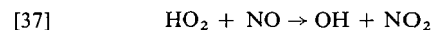


and

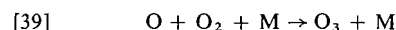


as sinks for tropospheric odd oxygen. Elsewhere,

Chameides and Walker (43) discussed a possible source of tropospheric odd oxygen through the reaction sequence



followed by



The relative importance of the sources and sinks represented by [35] through [39] depends on the branching of HO₂ between reactions 35 and 37. Reactions 35 and 36 could provide a height integrated sink for tropospheric O₃ of about 2×10^{11} molecules cm⁻² s⁻¹, comparable to the total flux of O₃ believed to emanate from the stratosphere (44, 45). As a consequence of the large rates for [35] and [36], the distribution of tropospheric O₃ may be directly affected by local chemistry. This conclusion, drawn earlier by Chameides and Walker (43) from a consideration of tropospheric source strengths, is in disagreement with conventional views which regard O₃ as a passive tracer, both in the lower stratosphere and troposphere.

NOTE ADDED IN PROOF: After completion of this work, we learned of a discussion of atmospheric chlorine by Stolarski and Cicerone which was in part presented at the IUGG meeting in Kyoto. Their article also appears in this issue of the Canadian Journal of Chemistry.

Nien Dak Sze made valuable contributions to the discussion of chlorine chemistry in this paper. We are indebted also to James Friend for a useful discussion and to Max Havlick for service beyond the call of duty in the preparation of this manuscript. The work was supported jointly by the Atmospheric Sciences Division of the National Science Foundation and the National Aeronautics and Space Administration under grant numbers GA 33990X and NGR 22-007-067 respectively to Harvard University.

Permission to reprint Figs. 1, 2, 3, and 4, which originally appeared in The Journal of the Atmospheric Sciences (ref. 15) is gratefully acknowledged.

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