Atmospheric Nitrogen Fixation by Lightning

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ABSTRACT

The production of nitrogen oxides (NO and NO₂) by lightning flashes has been computed from a model of gaseous molecular reactions occurring as heated lightning-channel air cools by mixing with surrounding ambient air. The effect of ozone (O₃) on the production of nitrogen oxides has also been investigated in this model and it has been found that the O₃ oxidizes NO to NO₂ mainly at the end of the cooling process. The maximum total global production rate of nitrogen oxides by lightning is estimated to be $\sim 6 \times 10^{12}$ molecules per second, or $14.4 \times 10^8$ tonnes of NO₂ per year.

1. Introduction

The inadequacies concerning the global balance of odd nitrogen (odd number of nitrogen atoms per molecule) in the troposphere and stratosphere were emphasized by Tuck (1976), and until recently established by Noxon (1976), it was uncertain that lightning could be considered as a possible major source of odd nitrogen in the troposphere. The present paper is not so much concerned with the global balance of odd nitrogen as with the mechanism of its production in the atmosphere by lightning. In the following sections a short summary of theoretical and experimental information on the characteristics of return stroke lightning is first presented, following which a plan is outlined for the calculation of the production of nitrogen oxides by lightning. The chemistry involved in the computation is outlined and the computational techniques, together with the results and sensitivity of the results to the reaction rate parameters chosen, are discussed. The dependence of the final answer concerning the amount of nitrogen fixed on the rate of mixing of the lightning channel air with the ambient atmosphere is considered and experimental evidence bearing on the mixing process is discussed. The estimate of nitrogen fixation reached in this study is finally compared with previous estimates and measurement.

2. Lightning channel development

Detailed characteristics of the lightning discharge pertaining to the development of the return stroke channel were summarized recently by Berger (1977), Golde (1977), Orville (1977b) and Hill (1977b). A lightning stroke is typically a 5 km long break-down path that conducts a peak current of 20–30 kA in a pulse that rises to its peak in approximately 10 μs and dies away to essentially zero in 100 μs. Although the breakdown is confined initially to a narrow (millimeter) channel, the radius of the heated channel grows rapidly, because of dissipation of energy and the occurrence of a shock, to ~6 cm by the time the luminosity of the channel has ceased (Orville, et al. 1974).

Theories of the growth of the lightning channel under the influence of the cylindrical shocks produced by the energy dissipated have been given by a number of workers, including Abramson et al. (1947), Braginskii (1958), Sakurai (1953) and Lin (1954). These theories made use of the approximation that energy is expended in a channel instantaneously and that the source has an infinitesimal initial radius (so-called line source). These theories were followed by a number of numerical simulations, including those by Troutman (1969), Colgate and McKee (1969), Hill (1971) and Plooster (1971), who attempted to introduce realistic lightning sources into the calculations. These corrections are nontrivial because, if energy is to be dissipated in channels of centimeter radii and in times of the order of 100 μs, then it is essential that a zonal structure of the channel be considered and that radiation and energy transport between the zones be accounted for.

Results from a simulation that included energy transport by radiation and conduction and a realistic input return-stroke current pulse are illustrated in Fig. 1. It is seen in this figure that the shock fronts (indicated at various times by the symbol S) are responsible for only small temperature rises (at the times shown) relative to the high temperatures in the channel produced by ohmic heating of the return stroke current flowing in the channel plasma. The
temperature and radius of a heated channel will depend on the energy dissipation $E_0$ per unit length of channel. Comparing the radius and temperature of the shock front with the radius and temperature of the ohmically heated channel clarifies the relative roles of the shock and the heated channel with respect to the nitrogen fixation chemistry. For times $> 10$ $\mu$s, those regions wherein the shock creates temperatures in excess of 500 K are later engulfed by the expanding hot channel which persists at temperatures in excess of that temperature obtained by the shock in that region. Because of this feature of the lightning channel development, it is clear that the shock cannot be regarded in our model as a mechanism for the production of NO and NO$_2$ through the process of heating of air by lightning.

3. Proposed mechanism for NO$_2$ production

A more favorable mechanism for the generation of NO and NO$_2$ than the shock mechanism in lightning exists in the heating of the channel air and in the "freezing-in" of the nitrogen oxides produced. The possibility of the freezing-in process exists because of the cooling of the channel air by mixing in with the surrounding colder ambient air. Such a process has already been discussed by Gilmore (1975) in connection with the production of NO$_2$ by a heated fireball from a nuclear detonation. Freezing-in is a process in which the temperature of a gas mixture is reduced sufficiently rapidly that the rates of certain depletion reactions are reduced. In the case of nitric oxide (NO) in air, for a mixture density of between 0.1 and 1.0 ambient air density, the concentration of NO is a maximum at $\sim$4000 K. Zel’dovich and Raizer (1967), Gilmore (1975) and others have determined that if an equilibrium air-NO mixture is cooled to below a temperature of approximately 2300 K in a time of less than a few seconds, then a large fraction of the original NO concentration is retained. However, in order to evaluate whether the proposed freezing-in process is valid in the case of NO$_2$ production by lightning, it is clearly important that the heating and cooling process in the lightning channel be adequately understood.

As shown by a number of experimenters, including Zhivlyuk and Mandel'shtam (1961), Salanave (1961), Prueitt (1963), Uman and Orville (1964) and Orville (1977b), the typical lightning channel reaches a thermodynamic equilibrium gas temperature of the order of 20 000 to 30 000 K in a few microseconds after the onset of a return stroke. Spectroscopic measurements of the heated channel temperatures have indicated that the plasma remains in thermodynamic equilibrium during its cooling to the lowest temperature that has been experimentally determined (≈10 000 K). Cooling during this phase of the lightning stroke, which occurs in $\sim$50 $\mu$s, may be attributed to a number of factors including expansion of the channel, inclusion into the channel of outer zones at lower temperatures and loss of heat by radiation.

After $\sim$100 $\mu$s, as shown by observations and simulations, the lightning-current and channel heating input have effectively ceased. Simulations indicate that the shock front has separated completely from the hot channel. From Plaister's (1970) generalized curves and for a typical energy dissipation of $1.5 \times 10^4$ J m$^{-1}$, it may be shown that the channel has returned to approximately atmospheric pressure at 200 $\mu$s and that the shock has reached a distance of $\sim$20 cm from the axis of the channel. However, at this stage the high temperature boundary lies at a radius of only $\sim$9 cm from the channel axis. The shock front heating has long since become insignificant.

The cooling of the residual hot channel following cessation of the return stroke current pulse has been studied in connection with the topics of multiple strokes and continuing strokes of lightning. In particular, Uman and Voshall (1968) have considered channel cooling between 10 000 and 3000 K as the basis for the persistence of the electrical conductivity of the channel between multiple
strokes. They estimated, for example, that a channel of over 4 cm radius at approximately 50 μs might take over 150 ms to relax from an initial temperature of between 8000 and 14 000 K to a final temperature of 3000 K. In this analysis, they considered only thermal conduction from the channel as the cooling mechanism. They suggested, however, that if both conduction and convection heat losses had been involved, they would have expected a channel of double the initial radius (or ~8 cm radius) to have reached the same final temperature in about the same time. Apart from neglecting convective losses, Uman and Voshall made the following approximations: 1) local thermodynamic equilibrium existed in the heated channel at all positions and at all times, 2) heat loss by radiation from the channel was negligible, 3) the pressure within and around the channel was always nearly atmospheric, and 4) conduction and air flow in the channel were radial. We concur with Uman and Voshall that these approximations appear reasonable, and we further maintain that when the channel air, or plasma, reaches the lower temperature bound of 3000 K, it is still in approximate chemical and thermal equilibrium, as shown by the arguments which follow.

As maintained by Uman and Voshall, electron-neutral and neutral-neutral equilibrium times in the temperature range from 10 000 to 3000 K are always less than 1 μs and, consequently, the kinetic energy in the channel air is equilibrated on a time scale short compared to 1 μs. Electron-ion equilibrium times are also so short that the electrons and ions have essentially the same temperature. In order to estimate the extent to which the equilibrium concentrations might conceivably be disturbed we start by assuming that the concentrations at 10 000 K are given by the well-known Gilmore values. Between 10 000 and 3000 K the two most abundant ions are e⁺ and NO⁺. With the reaction rate constant equal to -10⁻⁷ cm³ s⁻¹ for the recombination of NO⁺ and e⁻ according to the reaction, NO⁺ + e⁻ → N + O, the half-value depletion times of NO⁺ are 0.04 and 140 μs at 10 000 K and 3000 K, respectively. Further, considering the three-body recombination reaction, NO⁺ + e⁻ + e⁻ → NO + e⁻, with a reaction rate constant equal to approximately 10⁻¹⁹ cm⁶ s⁻¹, we find that the half-value depletion times are approximately factors of 10⁶ and 10 times faster, respectively, than the two-body values at 10 000 and 3000 K. Thus, it is reasonably certain that the electron-ion recombination reactions proceed sufficiently rapidly to keep the ion concentrations at near equilibrium values during a cooling process that takes tens to hundreds of milliseconds. Similarly, concerning the purely neutral-neutral reactions, we find that the three-body reactions occur on a time scale of the order of 1 μs or less. Between 10 000 and 3000 K, the three most important reactions are those forming the molecules N₂, NO and O₂, which are most favored from the high temperature bound in the order of their dissociation energies (viz., 9.76, 6.51 and 5.12 eV, respectively). The atom-atom recombination rate constants lie between 10⁻³⁴ and 10⁻³⁷ cm⁶ s⁻¹. At a temperature of 10 000 K, and for species concentrations given by equilibrium values, the characteristic recombination time for N + N → N₂ is ~1 μs for the reaction N + O → NO and N₂ is ~0.1 μs. Since the conclusion of Uman and Voshall's analysis was that multiple lightning strokes occur because the lightning channel takes of the order of 50 ms to cool from 10 000 to 3000 K, we infer from this cooling rate and from the above information on reaction times, that the channel medium exists during this cooling period in a state of reasonable chemical and thermal equilibrium.

4. Model for evaluation of NOₓ production

In an attempt to estimate the production of NOₓ by the typical lightning stroke, we have employed a simple model in which the air is heated initially in the lightning channel and then cooled by mixing with the surrounding ambient air. In principle, the mixing can commence at any temperature after the channel has cooled to approximately 10 000 K. Because information on the convective cooling of the lightning channel is completely lacking, we have in fact chosen to estimate what is probably the maximum NO production, for the following reasons: 1) Since we do not know how efficient the mixing is, we have assumed perfect mixing. 2) Since we do not know when convective mixing starts, we have chosen the starting point when the NO concentration in air is a maximum.

Equilibrium species concentrations in air at 3000 K were used as the starting point in our mixing calculations with the temperature of the outside mixing air at 273 K. Under the assumed initial condition that the pressures are the same inside and outside the heated channel, the above temperatures require that the density of the heated channel air be initially 0.949 ambient air density and under these conditions the NO concentration is close to maximum. Initial species concentrations in the heated air were obtained by interpolation between 0.01 and 0.1 ambient air density values at 3000 K. Temperatures and pressures of ambient air surrounding real lightning channels probably vary between about 230 and 300 K, and between about 1 and 0.5 atm.

In the model, temperatures of mixtures of unit volume of the initial hot channel air with incremental additions of perfectly mixed cold ambient air were computed from the heat capacities and the chemical reaction energies of the mixture, which were continuously determined. Thermal equilibrium
was assumed throughout, but the chemistry between existing species was followed according to the prevailing concentrations and the reaction rate constants appropriate to the continuously varying uniform temperature of the mixture. The computations were carried out for a number of arbitrarily chosen mixing rates of the cold and hot air components, and they were generally continued until the temperature of the mixture had approached ambient. The concentrations of individual species, including the nitrogen oxides NO and NO$_2$, were determined at all times and, in particular, the yields of NO$_2$ were obtained as functions of mixing rates and total mixing times. Details of the computations are given in the following sections.

5. Summary of reaction chemistry

The choice of chemical reactions which we believe are important in fixing nitrogen in a lightning stroke is based on our arguments that these reactions occur mainly in the hot lightning channel, that the induced shock wave has a negligible effect in the chemical process, and that interactions with ambient air responsible for producing thermal quenching begin when the channel is at $\sim 3000$ K. Under these conditions, the reactions of importance are between neutral molecules and atoms with insignificant contributions from charged species. In addition, we have omitted with the purpose of concentrating on the mechanism at this stage the influence of water vapor, hydrocarbons and other carbon-containing species on the chemistry of nitrogen fixation during the cooling of the hot channel. The effect of water may be important in the fixation process; but for the present study, we have only examined the dry air situation. In a future study, we intend to include the appropriate reactions involving water. Unfortunately, inclusion of water essentially triples the number of reactions currently being considered. To our knowledge, the effect of water vapor on the high-temperature chemistry which would exist in the heated lightning channel has not yet been studied by any investigators. [Note added in review: Chameides (1979) included chemistry of H$_2$O and CO$_2$ but found no effect on the NO and NO$_2$ concentrations at elevated temperatures.] The secondary effects of water vapor and rain on the nitrogen peroxide dispersed in the ambient air surrounding lightning have indeed been discussed; nevertheless, the relationship of the nitrogen oxide production by lightning and the existence, or non-existence, of nitrate and nitrite ions in storm precipitation remains unclear. We do not believe that CO$_2$ plays an important role in the lightning chemistry of dry air at the temperatures of interest to us. However, the effects of CO$_2$ on the heat capacity of the reaction system are taken into account. In wet air the CO$_2$ interacting with the water at high temperature may be an important source of hydrocarbons; and in future studies, this will be investigated.

It became clear early in the study that the role of ozone in the fixation process of the lightning channel should be investigated. This viewpoint is supported by the work of Donohoe et al. (1977) on the production of O$_3$ in pulsed discharges at one atmosphere pressure. Also, in agreement with the approach taken by Donohoe et al., the role of O (1D) in the ozone reactions was excluded on the grounds that the 1D state is very rapidly quenched to the 3P state when the particle density, as in the surrounding ambient air, is high.

In view of the constraints stated above, the chemical reactions included in our calculations are listed in Table 1. It should be noted that Reactions (1) and (2) in the above are the so-called Zel’dovich reactions (Zel’dovich and Raizer, 1967) which have been accepted by most investigators as an important pair of atom-molecule reactions in the high-temperature chemistry producing NO$_x$ from nitrogen/oxygen mixtures.

An extensive study of the reaction data relating to the processes involved in Table 1 was made, and the rates shown in the table appear to represent the best information presently available. The main source of these data is an NBS Special Publication (Hampson and Garvin, 1978). These data draw heavily on an earlier evaluation by Baulch et al. (1973). Other sources studied included works by Crutzen et al. (1978), Wofsy (1978) and the JANAF tables (1970).

Reaction data on ozone photoproduction and on ozone-NO$_x$ reactions have been obtained from Hampson and Garvin (1978), Crutzen et al. (1978) and Wofsy (1978). A tentative model of ozone production in lightning was also developed. It is clear that UV radiation will be strongly generated in the hot air channel, especially at the initial peak high temperatures of 20 000–30 000 K. Very tentatively, we estimate that at microsecond times there will be a significant percentage (~1%) of oxygen molecules, in a thin cool layer of ambient air surrounding the channel, which is photolyzed. It is also estimated that at microsecond times there may be as high as $10^{17}$ cm$^{-3}$ ozone molecules generated in this very thin layer, probably 0.1–1 mm in thickness, surrounding the lightning channel. The initial concentration of O$_3$ in Table 2 is intended to reflect the presence of this ozone. Orville (1967) has already observed spectroscopic absorption by ozone of the radiation emitted by the return current channel, but he was unable to determine the ozone's exact location. It will be apparent after the forthcoming discussion on computations and results that the effect of any model of ozone production on the NO$_x$ yield
### Table 1. Chemical reactions used in the simulation studies.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$k_f$</th>
<th>$k_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Principal reactions involving nitric oxide (NO)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>$N + O_2 \rightleftharpoons NO + O$</td>
<td>$6.6^{**}T \exp(-3150/T)$</td>
<td>$1.56^{*}T \exp(-19,450/T)$</td>
</tr>
<tr>
<td>2.</td>
<td>$N + NO \rightleftharpoons N_2 + O$</td>
<td>$1.6^{*}T \exp(-410/T)$</td>
<td>$7.8^{*}T \exp(-38,000/T)$</td>
</tr>
<tr>
<td>3.</td>
<td>$NO + NO \rightleftharpoons N_2O + O$</td>
<td>$1.3^{*}T \exp(-32,100/T)$</td>
<td>$1.2^{*}T \exp(-14,100/T)$</td>
</tr>
<tr>
<td>4.</td>
<td>$O + O + M \rightleftharpoons O_2 + M$ ([M] = 3[O] + [O]_2 + 0.5[N_2])</td>
<td>$1.4^{*}T^{-1} \exp(-171/T)$</td>
<td>$2.7^{*}T^{-1} \exp(-59,700/T)$</td>
</tr>
<tr>
<td>5.</td>
<td>$N + N + M \rightleftharpoons N_2 + M$ ([M] = [O]_2 + [NO] + [O])</td>
<td>$1.0^{*}T^{-0.5}$</td>
<td>$1.9^{*}T^{-0.5} \exp(-112,450/T)$</td>
</tr>
<tr>
<td>6.</td>
<td>$N + N + N_2 \rightleftharpoons N_2 + N_2$</td>
<td>$2.6^{*}T^{-0.5}$</td>
<td>$4.7^{*}T^{-0.5} \exp(-112,450/T)$</td>
</tr>
<tr>
<td>7.</td>
<td>$N + N + N \rightleftharpoons N_2 + N$</td>
<td>$2.26^{T^{-1.5}}$</td>
<td>$4.1^{*}T^{-1.5} \exp(-112,450/T)$</td>
</tr>
<tr>
<td>8.</td>
<td>$N + O + M \rightleftharpoons NO + M$ ([M] = [N] + [O]_2 + [N] + [O])</td>
<td>$1.0^{*}T^{-1.5}$</td>
<td>$3.8^{*}T^{-1.5} \exp(-75,000/T)$</td>
</tr>
<tr>
<td>9.</td>
<td>$N_2O + O \rightleftharpoons N_2 + O_2$</td>
<td>$1.2^{*}T \exp(-14,100/T)$</td>
<td>$6.0^{*}T \exp(-55,200/T)$</td>
</tr>
<tr>
<td></td>
<td>Principal reactions involving nitrogen dioxide (NO$_2$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>NO$_2$ + O $\rightleftharpoons$ NO + O$_2$</td>
<td>$5.5^{*}$</td>
<td>$1.7^{*}T \exp(-23,400/T)$</td>
</tr>
<tr>
<td>11.</td>
<td>N + NO$_2$ $\rightleftharpoons$ N$_2$O + O</td>
<td>$8.4^{*}$</td>
<td>$2.5^{*}T^{-2.5} \exp(-43,000/T)$</td>
</tr>
<tr>
<td>12.</td>
<td>NO + O + M $\rightleftharpoons$ NO$_2$ + M ([M] = [O]$_2$ + [NO] + [O] + [N]$_2$ + [N] + [NO]$_2$)</td>
<td>$1.1^{*}T \exp(940/T)$</td>
<td>$1.1^{*}T \exp(-33,000/T)$</td>
</tr>
<tr>
<td>13.</td>
<td>NO + NO + O$_2$ $\rightleftharpoons$ NO$_2$ + NO$_2$</td>
<td>$1.2^{*}T \exp(530/T)$</td>
<td>$2.0^{*}T \exp(-13,540/T)$</td>
</tr>
<tr>
<td></td>
<td>Principal reactions involving ozone (O$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>O + O$_2$ + M $\rightleftharpoons$ O$_2$ + M ([M] = 1.7[O]$_2$ + 1.6[N]$_2$ + [Ar])</td>
<td>$4.0^{*}T \exp(500/T)$</td>
<td>$9.9^{*}T \exp(-11,400/T)$</td>
</tr>
<tr>
<td>15.</td>
<td>O + O$_2$ $\rightleftharpoons$ O$_2$ + O$_2$</td>
<td>$1.1^{*}T \exp(-2300/T)$</td>
<td>$k_r/K_{eq} \approx 0$</td>
</tr>
<tr>
<td>16.</td>
<td>O + N $\rightleftharpoons$ NO + O$_2$</td>
<td>$3.0^{*}T \exp(-650/T)$</td>
<td>$k_r/K_{eq} \approx 0$</td>
</tr>
<tr>
<td>17.</td>
<td>O$_2$ + NO $\rightleftharpoons$ NO$_2$ + O$_2$</td>
<td>$5.4^{*}T \exp(-1200/T)$</td>
<td>$1.68^{*}T \exp(-25,400/T)$</td>
</tr>
<tr>
<td>18.</td>
<td>O$_3$ + NO$_2$ $\rightleftharpoons$ NO$_3$ + O$_2$</td>
<td>$7.2^{*}T \exp(-2450/T)$</td>
<td>$k_r/K_{eq} \approx 0$</td>
</tr>
<tr>
<td>19.</td>
<td>NO + NO$_2$ $\rightleftharpoons$ NO$_2$ + NO$_2$</td>
<td>$6.0^{*}T \exp(-700/T)$</td>
<td>$3.9^{*}T \exp(-12,000/T)$</td>
</tr>
</tbody>
</table>

* The units of the pre-exponential factors are cm$^6$ g mol$^{-2}$ s$^{-1}$ for termolecular and cm$^5$ g mol$^{-1}$ s$^{-1}$ for bimolecular reactions.

** This is a shortened form of $6.6 \times 10^6$ and is used for the numerical factors in the pre-exponential factors in order to save space in the table.

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is minor. The presence of ozone in the ambient air, however, is extremely important in the conversion of NO to NO$_2$ as discussed in the next section.

6. Summary of computation method, typical results and sensitivity analysis

The three main competing processes, after departure of the shock wave, for lowering the temperature of the lightning channel, include mixing with ambient air, radiation, and molecular conduction from the mixing zone to the ambient surroundings. Our simulation of the cooling process begins at a channel temperature of 3000 K and, as briefly stated earlier, treats the channel as a variable volume, constant pressure, adiabatic, perfectly mixed reaction zone into which ambient air is fed at a rate designated by a parameter $F_0$.Treating the process as adiabatic incurs neglect of radiation and molecular conduction losses of energy to the ambient surroundings. In a later paragraph, we justify our choice of an adiabatic zone by showing that energy...
losses through radiation and conduction to the ambient surroundings outside the heated channel zone are negligible compared to the energy consumption by the ambient air being brought into the mixing zone. Under these conditions, the following conservation equations based on an initial unit volume of heated air are given below.

**Energy balance**

\[
F_0 \rho_0 c_0 (T_0 - T) = V \left( \sum_{i=1}^{N} P_{i,c_i} \frac{dT}{dt} + \sum_{j=1}^{L} \Delta H_j R_j V \right). \tag{1}
\]

**Total mole balance**

\[
\frac{F_0 P_T}{R_g T_0} + \sum_{i} \sum_{j} V R_i \alpha_{ij} = \frac{dn_t}{dt}. \tag{2}
\]

**Mole balance on each species**

\[
\frac{F_0 P_T}{R_g T_0} + \sum_{j} \alpha_{ij} R_j V = \frac{dn_j}{dt}. \tag{3}
\]

**List of Symbols**

- $\rho_0$ ambient air density (g mol cm\(^{-3}\))
- $c_0$ mean heat capacity of air added [cal (g mol K\(^{-1}\))]
- $c_i$ heat capacity of $i$th species [cal (g mol K\(^{-1}\))]
- $P_{i,c}$ concentration of $i$th species (g mol cm\(^{-3}\))
- $\Delta H_j$ heat of $j$th reaction [cal (g mol\(^{-1}\))]
- $R_j$ $j$th reaction rate [g mol (s cm\(^{-3}\))]\(^{-1}\)]
- $P_T$ total pressure (dyn cm\(^{-2}\))
- $P_{i,0}$ pressure of species $i$ at ambient conditions (dyn cm\(^{-2}\))
- $R_g$ gas constant
- $T_0$ ambient temperature (K)
- $\alpha_{ij}$ stoichiometric coefficient
- $n_t$ total moles
- $n_i$ moles of species $i$
- $V$ reaction volume (cm\(^3\))
- $F_0$ mixing rate parameter (cm\(^3\) s\(^{-1}\)).

With time as the independent variable, Eqs. (1)–(3) were integrated numerically by use of the well-known Gear Code which is especially designed to handle stiff systems of equations (Gelinas, 1972). The reaction rates $R_j$ were obtained from the data in Table 1 and the initial and ambient conditions are listed in Table 2.

The concentration of ozone, both in the initial mixture and in the ambient air, requires special comment because of the role of ozone in the fixation of nitrogen. It is evident that an accurate assessment of ozone in the initial hot channel is not available. The value in Table 2 is an order of magnitude above the estimate suggested by the model of O$_3$ formation discussed earlier in the section. However, when this concentration is viewed as a parameter in the lightning simulation, the O$_3$ is observed to have no effect. Thus, identical NO$_2$ production curves were obtained for all values of initial O$_3$ concentrations ranging from zero to the upper value listed in Table 2. It is probable that any O$_3$ injected into the hot channel rapidly establishes an equilibrium with molecular and atomic oxygen. On the other hand, the O$_3$ in the ambient air dominates the results at long times. The amount of ambient O$_3$ increases in the hot channel as the channel cools. By the time the temperature drops below 1000 K, nearly all the entering O$_3$ generates NO$_3$ by Reaction (17). However, the concentration of ambient O$_3$ is insufficient to produce a noticeable effect until the temperature drops below 300 K.

In the numerical computation, the mixing parameter $F_0$, which is the feed rate of air to the perfectly mixed reaction zone in our simulation, was varied between 0.01 and 1000 cm\(^3\) s\(^{-1}\). The computations were conducted for simulation times of up to 300 s. At this time or earlier, depending on the value of $F_0$, the production of nitrogen oxides resulting from the lightning stroke and its subsequent cooling is essentially completed.

In Figs. 2–5 for $F_0$ values of 0.1, 1, 10 and 1000 cm\(^3\) s\(^{-1}\), respectively, the total amounts of NO and NO$_2$ and the temperature $T$ of the mixed zone are shown as functions of time between 1 $\mu$s and 300 s after the start of mixing. Curves A and B in each figure show the NO and NO$_2$ histories, respectively, in the absence of reactions involving ozone [these are Reactions (14)–(19) inclusive and are referred to henceforth as the “ozone reactions”]. Curves C and D illustrate the variations in NO and NO$_2$ production when the ozone reactions are included. Finally, curve T gives the temperature history during the cooling process.

For the case of $F_0 = 0.1$ cm\(^3\) s\(^{-1}\) as shown in Fig. 2, the cooling rate is sufficiently low that considerable NO is reconverted to N$_2$ and O$_2$, particularly for the period between 0.1 and 1 s after mixing with ambient air begins. Thus, over 43% of the initial NO is reconverted to the elements for this
cooling rate. At about 0.3 ms after mixing begins, the NO production actually starts to rise slightly above its initial value and at ~3 ms reaches a maximum which is ~6% above the initial value. This increase in NO production can be attributed to the fact that the system is not quite in chemical equilibrium at the initial 3000 K and thus adjusts itself in early times during the mixing process. Since the system of reactions moves in the exothermic direction, the temperature also rises during this period by as much as 2% or ~61 K above its initial value of 3000 K. It is interesting also to note in comparing curves A and C that including the O₃ reactions has only a slight but discernible effect on the NO production as a function of time, at least up to 100 s. After 1 s, when the temperature is about 1800 K, conversion of NO to NO₂ becomes the dominant path for the decline in NO production relative to its initial value. Note also that the NO₂ production is almost negligible until after 1 s and that the inclusion of the O₃ reactions has little effect on its production (compare curves B and D). Thus, for the period from 1 to 100 s, the NO removal is essentially stoichiometric in terms of NO₂ production and can be attributed mainly to Reaction (13) with lesser contributions from the reverse of Reaction (10).

A similar pattern of behavior occurs for $F₀ = 1.0$ cm³ s⁻¹ as shown in Fig. 3 except that, with cooling occurring more rapidly, only ~20% of the initial NO is converted to the elements. At ~0.1 s, transformation of NO to NO₂ becomes the dominant mode of NO loss via Reaction (13) and the reverse of Reaction (10). At 100 s, when the temperature of the mixing zone is approximately ambient, the O₃ reactions [mainly Reaction (17)] dominate the conversion of NO to NO₂. Again, the production paths of NO and NO₂ are essentially unaffected by inclusion of the O₃ reactions except when the temperature is near ambient.

In Fig. 4, the mixing rate is increased to $F₀ = 10$ cm³ s⁻¹ and the reconversion of NO to the elements amounts to only ~9% of its initial value. After ~10 ms, the mixing zone is cooled enough so that NO disappears mainly by conversion to NO₂; and after 1 s, the principal oxidation of the NO to NO₂ is via the ozone reactions. After 10 s, the O₃ effect becomes quite pronounced. It is also noteworthy that the increase in production of NO above its initial value as seen for the lower mixing rates does not appear at $F₀ = 10$ cm³ s⁻¹ in the absence of the O₃ reactions and occurs only very slightly when the O₃ reactions are included. Likewise, the temperature rise above the initial value of 3000 K is essentially nonexistent even when the O₃ reactions are included.

Finally, the fastest mixing rate corresponding to $F₀ = 1000$ cm³ s⁻¹ is shown in Fig. 5. In this case, the temperature rapidly falls to ambient ~10 ms. The reconversion of NO to the elements is less than 2% of its initial value. Thus, essentially all of the NO originally formed in the lightning stroke is frozen-in by the rapid cooling. In the absence of the ozone reactions, the conversion of NO to NO₂ is negligible for times up to 300 s. This is not surprising since, without O₃, the principal reaction at ambient temperature is the slow oxidation of NO by molecular oxygen. When the O₃ reactions are included, essentially all of the fixed NO is converted to NO₂ after 100 s of cooling time have elapsed as shown by curves C and D in Fig. 5. These curves are nearly...
Fig. 3. As in Fig. 2 except for $F_0 = 1.0 \text{ cm}^3 \text{s}^{-1}$.

Mirror images of one another with the main oxidation of NO being attributed to Reaction (17). Comparing Fig. 5 with Fig. 2, it is seen that the subtle variations in the NO production path which appear at very low cooling rates are essentially washed out at very high mixing rates.

Unlike a nuclear shock when the temperature is driven down again on the undercompression side in a time of the order of less than 1 ms, it is extremely improbable (except at extremely high $F_0$ values) in the lightning case that the mixed air will cool in a time even nearly approaching 1 ms. In fact, the observed cooling time of a lightning channel, as stated earlier, appears to be of the order of hundreds of milliseconds and longer. This rate of cooling is more nearly shown in Fig. 4 with $F_0 = 10 \text{ cm}^3 \text{s}^{-1}$ so that the temperature falls to ambient in $\sim 1$ s.

An important part of our study was to determine the sensitivity of the reaction system given in Table 1 to variations in the net rate of each reaction and in the initial concentrations of selected species. For the former case, the net rate of each reaction was arbitrarily set equal to zero in the Gear Code; and each time that this was done, the effect

Fig. 4. As in Fig. 2 except for $F_0 = 10 \text{ cm}^3 \text{s}^{-1}$. 
on the remaining system was computed in terms of NO and NO2 production versus time. This approach was considered the most appropriate because of the low sensitivity of NOx production to small changes in the reaction rate constants. Moreover, the ratios of the rate constants for forward and reverse directions of each reaction were consistent with the thermodynamic equilibrium constant for that reaction. With this thermodynamic constraint, it seemed inconsistent to us to modify the rate constant in one direction but not in the other. Since we wished to identify the key reactions which determine the qualitative behavior of the system, the elimination of reactions entirely by setting their net rates to zero provided more qualitative insight into the effects of each reaction than did the quantitative sensitivity factors obtained by small changes in the rate constants. It was found from this analysis that the system was significantly sensitive to Reactions (1), (2), (9), (11) and (12) and relatively insensitive to net rate changes in the remaining reactions. The effects of separately setting the net rates of Reactions (1), (2), (9), (11) and (12) equal to zero are shown in Fig. 6. It is clear from this figure that, among these five reactions, the system is the most sensitive to Reactions (2) and (9) relative to NO and NO2 production from lightning. Without Reaction (2), all of the NO produced in the initial hot channel is preserved in the cooling process and ultimately becomes NO2. Without Reaction (9), approximately 45% of the NO relative to its initial amount is lost with ~30% reverting back to N2 and O2, while ~15% is converted to NO2 during the cooling process for $F_0 = 10$ cm$^3$ s$^{-1}$.

In determining the sensitivity to initial concentrations of selected species (excluding N2, O2 and O), the initial concentration of NO was increased by a factor of 2 and all other initial concentrations of species (N, NO2, CO2 and A) were increased by a factor of 10. Except for the NO, the change in the initial concentration of any one species had no discernible effect for cooling times $> 1$ ms. The doubling of the NO concentrations caused an increase in the fixed NOx of only 13%, probably due to relaxing to equilibrium.

7. Examination of the mixing-rate problem

In attempting to establish a realistic value of $F_0$ for our simulation, we first comment on other processes in competition with mixing which help to reduce the temperature of an actual lightning channel. As stated earlier the other processes besides mixing with air are radiation from the channel and molecular conduction from the mixing zone to the ambient surroundings. Our simulation, which neglects these latter two processes, says that, when $F_0 = 0$, the lightning channel stays at 3000 K forever. If we remove the adiabatic restriction and keep $F_0 = 0$, we can approximate the combined cooling rate by conduction and radiation. We have approximated that rate by assuming that the emissivity and molecular thermal conductivity of air are applicable and equal to their values at 3000 K, viz., 0.003 and $9 \times 10^{-4}$ cal (cm K)$^{-1}$, respectively. We find that, in a time interval of 0.2–1 s, these processes will reduce the temperature of a typical lightning channel at 3000 K by $\sim 500$ K, which would correspond to an $F_0$ value of $\sim 0.1$ cm$^3$ s$^{-1}$ in our adiabatic simulator. This loss, which is mainly by thermal conduction, means that our model is reasonably acceptable.
down to a mixing rate of 0.1 cm³ s⁻¹, but is certainly not valid at extremely low mixing rates of 0.01 cm³ s⁻¹ and less. In what follows, we establish what we believe is a realistic estimate of \( F_0 \). One estimate is calculated by determining for each \( F_0 \) the time required to disperse throughout a storm the NO produced by a lightning stroke. This time requirement is compared to Noxon's (1978) observation of NO₂ in a 27 km² storm of 1 h duration with an observed stroke rate of five strokes per minute. The assumption that Noxon observed uniformly distributed NO₂ corresponds to an approximate value of \( F_0 = 10 \) cm³ s⁻¹ in our adiabatic simulator. The reaction time required for ambient ozone to oxidize NO to NO₂ is short (of the order of a minute) compared to the time required to disperse the contents of the lightning channel.

A second estimate of \( F_0 \) is obtained by using photographic evidence, referred to later in Fig. 7, to estimate the persistence of the heated channel. For a persistence of the channel (vis-a-vis turbulent cooling) of ~0.1 s, this estimate of the cooling rate parameter \( F_0 \) is again approximately equal to 10 cm³ s⁻¹.

8. Estimates of NO₂ production

An estimate of the production of NO by the heating mechanism proposed requires a number of input data, including 1) the amount of heated air produced by a typical lightning flash; 2) the concentration of NO in the channel air before cooling and the efficiency of the quenching-in process after cooling to ambient temperature; and 3) the data on the global frequency of lightning flashes for assessing the global production.

The above three requirements are discussed below under a number of related subheadings.

a. Amount of heated air produced per stroke

Since we have considered the nitrogen fixation process as commencing at an initial temperature of 3000 K, we require information on the amount of air in the lightning channel at approximately this temperature. Lightning flashes usually consist of a number of individual return strokes, separated on the average by ~40 ms. Although there are very large variations in the number of strokes per flash, as there are in the times between strokes, the average number is probably three. In what follows, the probable amount of air heated in a single stroke is first discussed and then an attempt is made to extend this value to a number of strokes, as in a flash.

For a number of years, following Schonland's (1937) photographic measurements, the luminous lightning channel was accepted as having a radius of between 7 and 12 cm. In the 1960's (see Berger, 1977) a number of measurements, derived from the effect of lightning on "electrodes" at the base of strokes, appeared to indicate that the channel diameters were measured in millimeters. The reasons for the differences in the two methods have been discussed in a number of places (e.g., Orville et al.,
1974), and it is now generally recognized that the electrode contact method does not give true values of the lightning channel size in air. Photographic measurements, however, can also overestimate the channel size. As Orville et al. (1974) noted, photographic images have to be corrected for overexposure and for spreading of the photographic emulsion. After applying corrections for these effects, Orville et al. measured a channel radius of 6.5 cm in a single stroke of lightning, at the end of its luminous phase. From Orville (1977b), one expects that the channel remains luminous up to ~50 μs after stroke onset. Although accurate simulations of the lightning channel have not been carried out to very late times, some approximate calculations by Plooster (1970) may be used to estimate the radii of the hot channel regions at times approaching 5 ms. Plooster’s curves are given for generalized radii and times related to the energy input $E_0$ per unit length of lightning channel. We choose a typical value of $E_0$ equal to $10^8$ J m$^{-1}$. [This value is approximately an order of magnitude less than many earlier choices for a typical stroke; however, in a recent review of lightning energy estimates by Hill (1979), $10^8$ J m$^{-1}$ was selected as the preferred value measured by four independent methods.] Plooster’s curves give 12 cm for the radius of a hot channel at 5 ms. This value is significantly larger than Orville et al.’s but is expected to be so since this radius occurs at a later stage in the channel development than when the temperature is 10 000 K and barely luminous.

Another estimate of channel size at very late times can be obtained by assuming that the energy in the channel at 3000 K is fixed by the lightning energy deposition. Although there have been different estimates of the energy propagated from the channel as a shock wave, the two simulations of lightning channel development by Plooster (1971) and Hill (1971) indicated that only ~10% was lost in this manner. A certain amount of deposited energy is also lost by radiation. For times < 100 μs, when the channel temperatures are between approximately 25 000 and 10 000 K, most of the radiation from the channel is in the UV and visible bands. The UV, however, is absorbed in the air surrounding the channel within tenths of millimeters. This radiation is therefore not lost but contributes ultimately to heating of the channel. In the case of the visible and the short wavelength IR (4000–11 000 Å) it has been found that the total amount of energy radiated over the whole duration of the channel is only about 600 J m$^{-1}$. The amount of IR radiated beyond 11 000 Å, when the temperature has fallen below ~10 000 K, is assumed to be small and is neglected. This assumption was made originally by Uman and Voshall (1968) who estimated that the radiation loss would be negligibly small compared to the thermal diffusion loss from the channel during this phase. Thus, if the typical deposited energy is 10 000 J m$^{-1}$, it is expected that the amount of residual energy in the channel is ~8400 J m$^{-1}$. This energy is essentially the heat retained in the channel at the initial temperature of 3000 K. Assuming that the air obeys the perfect gas law, and assuming that the pressure inside the channel is the same at this temperature as outside in the ambient atmosphere (assumed to be 10^6 erg cm$^{-3}$) then the volume per unit length of the channel, considered to be cylindrical, is $\pi r^2 = (8.4 \times 10^7)/10^6$ cm$^2$, i.e., the channel

![Fig. 7. Photograph of ribbon lightning. The original was taken by T. L. Morgan in Oswestry, England. Other reproductions of the whole flash have been published by Golde (1967) and Orville (1977). The flash consisted of at least nine strokes that probably occurred over a total time of 0.35 s. The purpose of reproducing the photograph here is to illustrate the long-time persistence of the original lightning channel (indicated by the darkest trace at the left of the photograph).]
radius $r \approx 16.2$ cm at the commencement of convective cooling. This radius appears consistent with the earlier estimates since the time involved in reaching it is longest and one would expect its value to be the largest.

b. Increase of heated air due to a flash

A difficult factor to estimate is the increase in the amount of heated air produced by a flash, as distinct from the amount produced by a stroke. As shown by the accompanying photograph (Fig. 7), a lightning channel is evidently not appreciably distorted by the delays between strokes. By analogy, therefore, it would appear that the channel is only "pumped up" by the successive strokes to a final radius corresponding to the total deposited energy in the flash. As far as the production of NO$_x$ is concerned, however, this viewpoint is somewhat oversimplified because much of the same air in the channel is only reheated and cooled by successive strokes.

The assessment of NO$_x$ production due to a flash is also complicated by the fact that not all of the strokes have the same energy. One statistic of typical lightning gives 4.5 C as the charge transferred by a first stroke, followed by two subsequent strokes each of 0.95 C. If we accept Plooster's (1971) rule that the energy in a stroke is proportional to the 0.45 power of the charge deposited, then the ratio of energies in the first and a subsequent stroke is approximately 2:1. For a three-stroke typical flash, therefore, it might be expected that the amount of air heated in a flash is between a factor of approximately 1 and 2 times the air heated in a single stroke: an average value is therefore probably $1.5 \pm 0.5$.

c. Cooling efficiency factor

As determined in the model analysis, the production of NO$_x$ as a function of the rate of cooling appears to be between 1 and 0.5 times the initial amount of NO at 3000 K for approximate cooling times between about 1 ms and 10 s. Although information on cooling of lightning channels below about 10 000 K is practically nonexistent, there are, however, a number of photographs showing that lightning channels persist intact through many multiple strokes lasting up to the order of a few seconds (see Workman et al., 1960). This information can be interpreted as indicating that the cooling of the lightning channel is relatively slow, but it may also mean that only the axis of the channel persists between strokes or that the channel persists for long times only if multiple strokes occur. The model does not presently answer the cooling rate factor; however, it suggests that the efficiency factor corresponding to our preferred value of a mixing rate equal to 10 cm$^3$ s$^{-1}$ is probably ~0.9. This factor could probably vary between the limits of 1.0 and a lower limit of ~0.6. This lower limit corresponds to an $F_0 = 0.1$ which in turn corresponds to a cooling time of several seconds to reach 2000 K.

d. Estimate of NO$_x$ yield

Equilibrium air compositions indicate that the NO concentrations existing at $p/p_0 = 0.1$ (where $p_0$ is the ambient gas density at 273 K) are approximately $9 \times 10^{16}$ and $1.05 \times 10^{17}$ cm$^{-3}$ at temperatures of 3000 and 4000 K, respectively. The maximum NO concentration subject to a pressure equilibrium condition of one atmosphere inside and outside the lightning channel actually occurs at a temperature slightly below 3000 K and the concentration value is approximately $1.1 \times 10^{17}$ NO$_x$ molecules cm$^{-3}$. This condition corresponds closely to the one chosen for the model of our investigation. The cooling rate efficiency value is therefore estimated to equal 0.9 and the yield of NO$_x$ after cooling is approximately at $1.0 \times 10^{17}$ NO$_x$ molecules cm$^{-3}$ of the original lightning-channel air at 3000 K.

In order to estimate a value of the NO$_x$ yield per lightning flash or to obtain an estimate of the NO$_x$ global yield we have selected the following preferred values of lightning characteristics:

- Energy of first stroke = $10^4$ J m$^{-1}$
- Radius of heated air channel (at 3000 K) due to first stroke = 16 cm
- Increase in channel volume due to typical flash = 1.5
- Length of channel = $5 \times 10^6$ cm
- Volume of heated air (at 3000 K) due to complete flash = $6 \times 10^8$ cm$^3$
- Maximum number of molecules of NO$_x$ in air cooled to ambient temperature = $1.0 \times 10^{17}$ molecules per cubic centimeter of the original lightning-channel air at 3000 K.
- Maximum total number of NO$_x$ molecules produced per flash = $6 \times 10^{25}$ molecules
- Global flash rate (Edgar, 1978; Orville and Spencer 1979) = 100 s$^{-1}$
- Maximum total global NO production rate = $6 \times 10^{27}$ molecules s$^{-1}$.

This estimate of the global production rate could be subject to a considerable error due to uncertainties in input data. For example, the volume of the original heated channel air at 3000 K could be in error by a factor of between 3 and 1/3, arising from the uncertainty of $E_0$ (assumed to be between a factor of 2 and 1/2) and from the uncertainty of the correction for the multiplicity of lightning strokes (assumed to be between a factor of 3/2 and 2/3). The uncertainty in the cooling efficiency factor (i.e.,
0.9) is not expected to be larger than approximately between the limits of 1.0 and 0.6. The uncertainty in the global flash rate value probably lies between a factor of 2 and 1/2 of the value assumed. As a consequence of these uncertainties, the estimated global production rate could be uncertain to within a factor of between approximately 8 and 1/8 of the value given. It is of interest to note that most of this uncertainty arises from the possible errors in the stated characteristics of lightning.

**e. Comparison of NO$_2$ production rates**

Noxon (1976) estimated the NO$_2$ production rate to be $\sim 10^{26}$ molecules per stroke; however, we believe that Noxon's terminology suggests that "stroke" was probably synonymous with our term flash, since he discussed observing five strokes per minute occurring within 3 km of the observatory and since it would not appear possible that Noxon could distinguish between a single stroke event and a flash of multiple strokes merely by visual observations.

In relation to a comparison between yields of NO$_2$ and NO, we would also expect that all of our NO would be converted to NO$_2$, on a molecule-for-molecule basis, within minutes after being dispersed from the cooled lightning channel. We therefore claim that we can compare Noxon's numbers of NO$_2$ molecules with our numbers of NO$_2$ molecules on a one-to-one basis. Noxon's value of the NO$_2$ production rate is thus approximately 50% larger than our NO$_2$ production rate of $6 \times 10^{25}$ molecules per flash. This result is somewhat conflicting since we would expect our value to represent a maximum production rate. There nevertheless appears to be enough uncertainty in Noxon's value, stated to be possibly an order of magnitude, to encompass the production rate value given in our estimate.

Chameides et al. (1977) estimated that the production of NO$_2$ (mainly NO) would be equal to $6 \times 10^{16}$ molecules per joule of lightning stroke energy. If we choose a preferred value of $10^4$ J m$^{-1}$ and a typical lightning path length of 5 km for the characteristics of a single lightning stroke, we find that the yield per stroke from Chameides et al.'s data is equal to $3 \times 10^{24}$ molecules. Thus, for a flash, which increases this value, as in our case by a factor of 1.5, Chameides et al.'s value is $4.5 \times 10^{24}$ molecules of NO$_2$ per flash. This yield is approximately 13 times less than the value we estimated for a flash. The choice of $10^4$ J m$^{-1}$ for a typical stroke dissipation made by Chameides et al., although too large in our estimation, would bring their value closer to the yield observed by Noxon but would also increase our value by approximately an order of magnitude. [Note added in review: Chameides (1979) now suggests a production yield of $(8-17) \times 10^{16}$ molecules of NO$_2$ per joule of lightning energy. This yield is between 10 and 5 times less than our estimate.]

The practice of expressing NO$_2$ yields in terms of production per joule of expended lightning energy, as was done by Tuck (1976), Griffing (1977) and Chameides et al. (1977), appears to us to confuse the issue of the fixation of nitrogen by the lightning process. Thus, it is not clear whether N$_2$O should be included in the energetics-production statement, since it appears that N$_2$O is not produced to any large extent in the lightning channel but may be produced (if Donohoe et al.'s findings of N$_2$O production in a brush discharge are confirmed for lightning) in the corona surrounding the lightning channel. Noxon has also claimed that NO$_2$ is not produced in the lightning corona. Further, as Colgate and McKee (1969) and Hill (1979) have discussed, there is reason to believe that a considerable fraction of the total energy in a lightning discharge is expended in the atmosphere surrounding a lightning channel, at the same time as energy is dissipated in the lightning stroke.

Finally, it is relevant to note that based on the volume of the spark filament used, the NO$_2$ yield observed by Donohoe et al. (1977) was equivalent to a production of $9 \times 10^{16}$ molecules of NO$_2$ cm$^{-3}$. This is only approximately 50% larger than the production of NO$_2$ (molecules cm$^{-3}$) estimated in our investigation. Because a strong air flow was used, the Donohoe et al. cooling and collection efficiency was close to unity. We consider the Donohoe et al.'s experiment as strong independent evidence in support of the NO$_2$ production determined in our investigation.

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