

# Nitrogen Oxides, Nuclear Weapon Testing, Concorde and Stratospheric Ozone

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Although amounts of nitrogen oxides equivalent to the output from many Concorde were released into the atmosphere when nuclear testing was at its peak, the amount of ozone in the atmosphere was not affected.

At present the ozone layer, which is centred at a height of about 25 km in the stratosphere, is not completely understood. At one time it was thought that the oxygen reactions alone, the so-called Chapman classical theory, could account quantitatively for the observed ozone profiles. But as knowledge of the relevant rate coefficients and the natural distribution of ozone became more exact, it became apparent that the classical theory gave theoretical ozone profiles with a total ozone content much greater than that observed. This discrepancy was for a while accounted for by turning to the so-called "wet chemistry" thesis—that reactions involving water and its dissociation products were responsible for a higher ozone destruction rate than that of the classical theory. Again better measurements of the relevant chemical rate coefficients led to the fall of this explanation from favour. The current suggestion<sup>1,2</sup> is that naturally occurring nitrogen oxides in the stratosphere, possibly originating from the troposphere and high atmosphere, may play a significant role in the conversion of stratospheric ozone and atomic oxygen to molecular oxygen. It would seem<sup>3</sup> that a concentration of 1 to 10 parts per 10<sup>9</sup> of nitric oxide in the stratospheric air is required to produce agreement between measurement and the nitrogen oxide photochemical theory. The actual amounts of nitric oxide in the stratosphere have yet to be established.

It is in this context that there has been much speculation recently<sup>3-5</sup> that the oxides of nitrogen produced in the combustors of the jet engines of high flying supersonic aircraft could interact with, and so attenuate, the Earth's ozone shield and increase the ultraviolet radiation reaching the planetary surface. It is fair to say that none of these papers contains the necessary full, quantitative consideration<sup>6</sup> of the interaction of radiation, photochemistry and the atmospheric circulation. It is, however, incontrovertible that in laboratory conditions NO and NO<sub>2</sub> convert ozone and oxygen atoms to molecular oxygen. Such considerations have resulted in the initiation of a number of research programmes in the United States, Britain and France to study the climatic consequences of the operation of fleets of supersonic aircraft.

Any process which heats air above ~2,300 K will produce significant quantities of NO as an equilibrium constituent. Examples of such heating include the shock waves from nuclear explosions as well as the operation of the combustion chambers of aircraft jet engines. The actual amount of nitrogen oxides remaining at ambient temperatures will

depend on the rate at which the heated air cools through the 2,500 K temperature region. It may be that massive amounts of nitrogen oxides have already been injected into the stratosphere during the various nuclear testing programmes.

## Shock Wave

In order to calculate the amounts of nitrogen oxides produced in the shock waves of nuclear explosions, it is necessary to know the pressure-temperature history of each parcel of air through which the shock front passed. We used the mathematical description of the spherical shock wave given by Taylor<sup>7</sup> to calculate the pressure-temperature histories of seven spherical surfaces enclosing fixed masses of air around the explosion centre. We then obtained values of pressure and temperature of each spherical shell enclosed by these seven surfaces by averaging the values at the two boundaries. The innermost shell (1), which includes the explosion centre, was taken to have the temperature and pressure history of the first spherical boundary. This was carried out for explosions of 1, 10 and 60 Mton TNT equivalent. The results of these calculations are given in Fig. 1.

Zel'dovich and Raizer<sup>8</sup> point out that the theory is not strictly applicable to the central regions of the explosion (shells (1) and (2)) where radiative effects probably dominate. Also the theory becomes more approximate when the pressure in the shock front is less than about ten times that of ambient.

In arriving at the curves in Fig. 1, a constant value, 1.4, of the ratio of specific heats  $\gamma$  has been assumed. Although at higher temperatures,  $\gamma$  is reduced from its ordinary tropospheric value of 1.4 by the absorption of energy in the form of molecular vibrational quanta, at very high temperatures increasing dissociation may be expected to compensate for this effect. Taylor noted that his calculations fitted the observed behaviour of the fireball in the first nuclear test in New Mexico better for  $\gamma=1.4$  than for  $\gamma=1.3$ . The shock wave has been assumed to propagate spherically in a uniform atmosphere at 290 K and 1,000 mbar. For the largest explosion considered (60 Mton), the radius of the 2,000 K surface is about 3 km, at which height this approximation is acceptable as demonstrated by Korobeinikov's more accurate description<sup>9</sup> of shock wave propagation in a real atmosphere.

## Chemical Kinetics of Heated Air

The production of NO in shock-heated air has been directly measured in laboratory shock tube experiments at temperatures between 2,300 K and 6,000 K by Camac and Feinberg<sup>10</sup>.

Mole fractions of nitric oxide,  $[\text{NO}]/[\text{M}]$ , of up to 0.1 were observed; the experiments applied, however, to short reaction times (several microseconds) and pressures from 0.01 to 0.07

a particular air mass, through its pressure-temperature history as a function of time down to times and temperatures where the NO production and destruction rates are slow compared to the cooling rate.

The elementary chemical processes used in calculating the nitrogen oxide production in the hot air masses created by the nuclear shock wave are as follows.

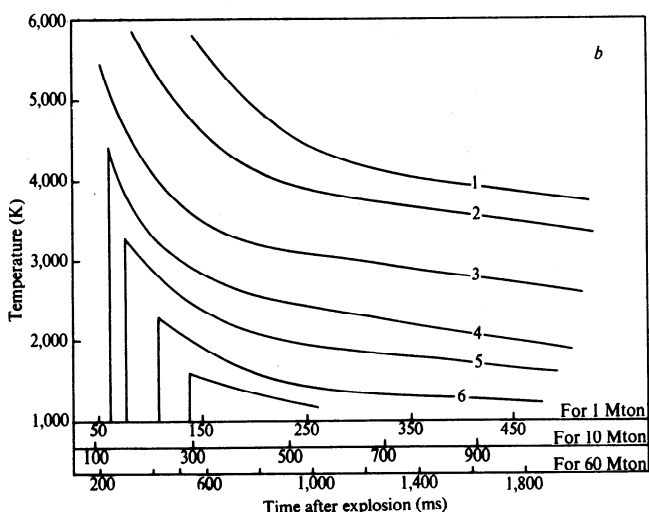
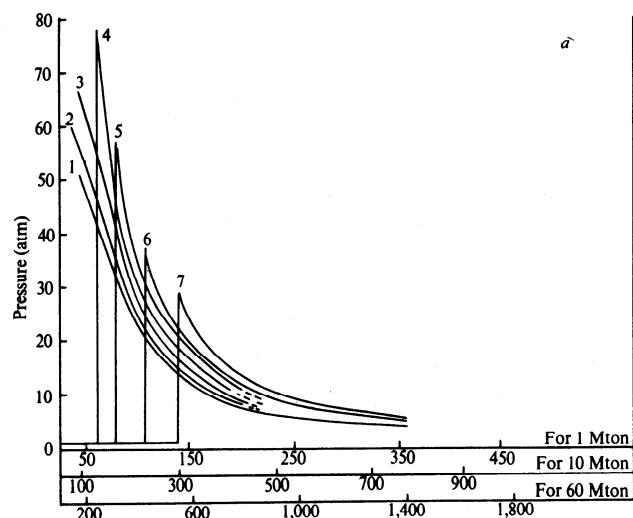
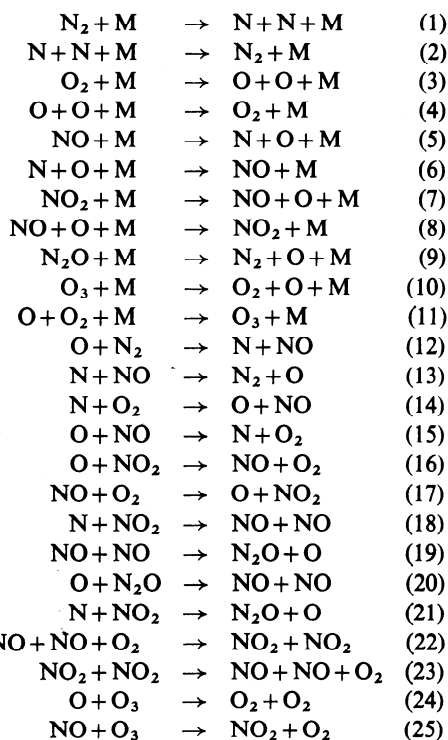


Fig. 1 Pressure (a) and temperature (b) histories for seven shells due to the shock wave around 1, 10 and 60 Mton explosions. Masses in units of  $10^{12}$  g per shell are

Shell No	1 Mton	10 Mton	60 Mton
1	0.115	1.15	6.9
2	0.115	1.15	6.9
3	0.103	1.03	6.2
4	0.075	0.75	4.5
5	0.145	1.45	8.7
6	0.273	2.73	16.4
7	0.283	2.83	17.0

atm. This is in contrast to the conditions following a weapon burst, where, after a few hundred milliseconds, pressure relaxation rates are of the order of  $50 \text{ atm s}^{-1}$  and cooling rates are of the order of  $2,000 \text{ K s}^{-1}$ . The masses of the concentric shells of air heated above 2,000 K are typically of the order of  $10^{12}$  g. In these circumstances the best *a priori* way to calculate production of nitrogen oxides would be to start with a chemical kinetic mechanism composed of the elementary processes thought to be relevant and derive the set of simultaneous differential equations describing the variation in time of the number densities of the molecular species involved. These equations should then be solved, by numerical integration, for



Excited species of both atoms and molecules have not been included, though some, for example  $\text{O}(^1\text{D})$ ,  $\text{O}(^1\text{S})$ ,  $\text{O}_2(^1\Delta)$ ,  $\text{O}_2(^1\Sigma_g^+)$ ,  $\text{N}^2(\text{D})$ ,  $\text{N}_2(\text{A}^3\Sigma_u^+)$ ,  $\text{N}_2(\text{B}^3\Pi_u)$ ,  $\text{NO}(\text{A}^4\Pi)$  and  $\text{NO}(\text{A}\Sigma^2)$ , may be expected to be populated or chemically produced at the higher temperatures. Justification for this omission is that the pressures which accompany the high temperature ensure that collisional deactivation of excited species is likely to be efficient. Also possible coupling between molecular motions, chemical processes and the kinetic energy of the shock wave in the air immediately behind the shock front has been considered to be negligible because a comparison of the time taken for the shock to traverse the thickness of the shock front (a few mean free paths) and the time scale of the chemistry indicates that absorption of energy from the shock by chemical processes has but a small effect upon the shock front velocity in those regions where radiation effects are unimportant.

The integrations were carried out using rate coefficients taken from recent authoritative reviews as summarized in Table 1. With the exception of reactions (3) and (4), the rate coefficients have been adjusted for molecular nitrogen as the third body M. For reactions (3) and (4), the larger third-body efficiencies of atomic and molecular oxygen were used. Where the reverse process of a reaction occurred, values were chosen to be compatible with the thermochemical equilibrium constant.

The integrations were carried out by a semi-implicit scheme, programmed in ASSEMBLER, a low level IBM language. Initially, a simple Euler first-order forward time step method was used to perform the integration. A prohibitively small time step of  $10^{-10}$  s was required by this method. By setting nitrogen atoms and ozone to equilibrium, this was lowered to  $5 \times 10^{-7}$  s for shell (6), with its temperature of 2,300 K. The semi-implicit method could run satisfactorily, without setting any species to equilibrium, using a timestep of  $10^{-6}$  s at 2,300 K,

$5 \times 10^{-7}$  s between 2,300 K and 3,300 K (shell (5)), and  $10^{-7}$  s between 3,300 K and 4,400 K (shell (4)). The results obtained by the different methods at 2,300 K agreed closely; to have run the forward time step method at higher temperatures would have involved setting nitric oxide itself to equilibrium, thus defeating the purpose of the exercise. The semi-implicit scheme used the relation

$$Y_{n+1}(i) = \frac{Y_n(i) + P(i)\Delta t}{1 + Q(i)\Delta t}$$

where  $Y_{n+1}(i)$  is the concentration of the  $i$ th constituent at the  $(n+1)$ th time step and  $P(i)$  and  $Q(i)$ , functions of rate coefficients and concentrations of other species, are defined by the general chemical kinetic differential equation

$$dY(i)/dt = P(i) - Q(i)Y(i)^m$$

where in this case  $m=1$  or 2. At every time step each species was advanced in turn by this method, while the remainder were held constant. This method does not simultaneously solve all the continuity equations, and so cannot be guaranteed

**Table 1** Rate Coefficients

Reaction	A	N	E	Reference
1	$3.73 \times 10^{21}$	-1.6	224,900	11
2	$2.25 \times 10^{21}$	-1.6	0	11
3	$4.79 \times 10^{18}$	-1.0	118,700	13
4	$2.38 \times 10^{17}$	-1.0	340	13
5	$2.27 \times 10^{17}$	-0.5	148,830	14
6	$6.45 \times 10^{16}$	-0.5	0	14, 12
7	$1.54 \times 10^{16}$	0	65,000	14
8	$1.47 \times 10^{15}$	0	-1,870	14
9	$1.30 \times 10^{15}$	0	58,000	15
10	$3.89 \times 10^{14}$	0	22,720	13
11	$6.46 \times 10^{12}$	0	-2,100	13
12	$1.36 \times 10^{14}$	0	75,400	14
13	$3.10 \times 10^{13}$	0	334	14
14	$6.43 \times 10^9$	+1.0	6,250	14
15	$1.55 \times 10^9$	+1.0	38,640	14
16	$1.00 \times 10^{13}$	0	600	14
17	$1.00 \times 10^{12}$	0	45,500	14
18	$3.60 \times 10^{12}$	0	0	14, 16
19	$9.40 \times 10^{11}$	0	66,000	14
20	$2.50 \times 10^{13}$	0	26,900	14
21	$1.20 \times 10^{12}$	0	0	14, 16
22	$2.43 \times 10^9$	0	-1,046	14
23	$4.00 \times 10^{12}$	0	26,900	14
24	$1.20 \times 10^{13}$	0	4,790	13
25	$5.72 \times 10^{11}$	0	2,460	34

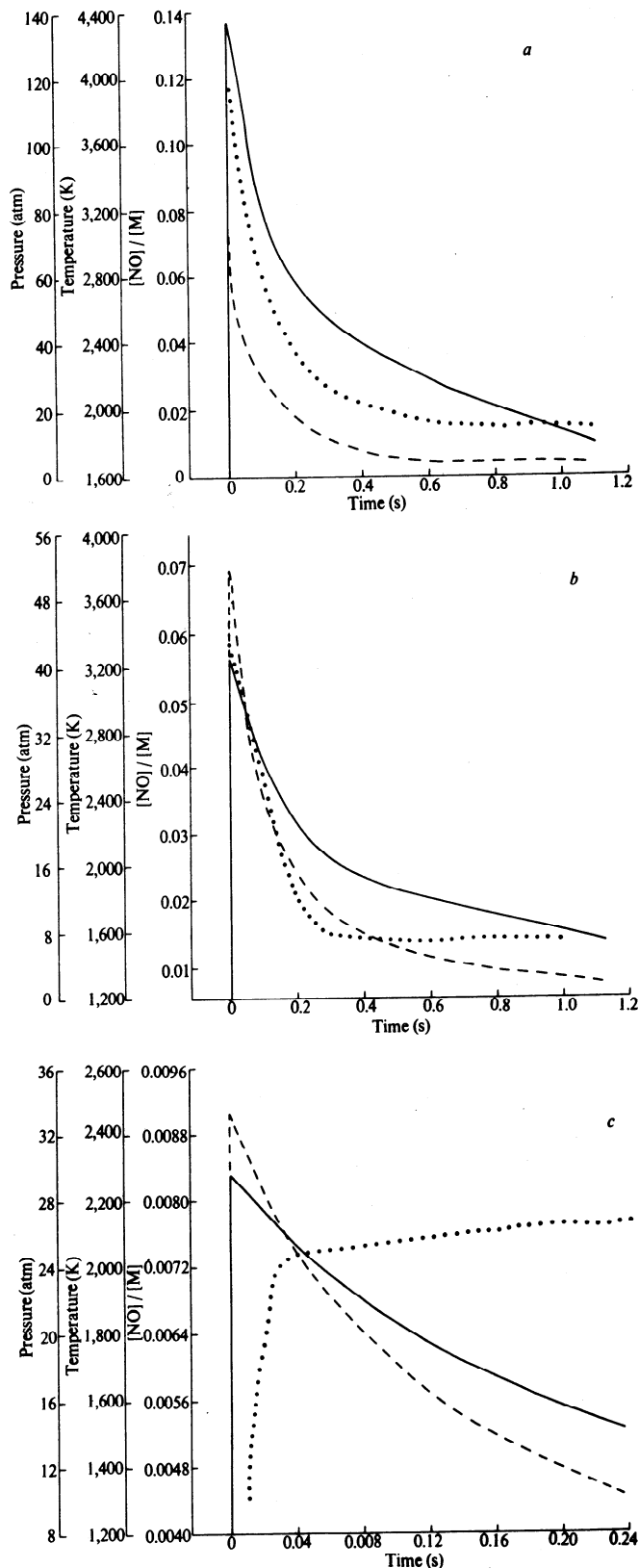
$$k = AT^n \exp(-E/1.987T)$$

$k$  is in  $(\text{cm}^3 \text{mol}^{-1})^n \text{s}^{-1}$  units;  $E$  is in  $\text{calorie mol}^{-1}$ . ( $n=1$  for a two-body process and  $n=2$  for a three-body process).

to conserve chemical identity (that is to say the total numbers of oxygen and nitrogen atoms). Chemical conservation was in fact obeyed quite well except in the few integrations which went to numbers of time steps greater than about  $2 \times 10^6$ . In all cases, however, results are quoted from integrations where conservation of N atoms and of O atoms was ensured by scaling after each time step to the density implied by the pressure and temperature history derived from Taylor's equations. Results of typical integrations are shown in Fig. 2. The rate coefficients were recalculated at descending 50 K intervals, after assuming a step perturbation of air from STP to the initial pressure and temperature values on each of the curves (4), (5) and (6) of Fig. 1. The air in the outer shell (7) (curve (7)) never reaches a high enough temperature to produce significant amounts of NO.

The results of these calculations are given in Table 2 in which the nitric oxide yield for each concentric shell is listed, together with the total air mass in that shell for explosions of 1, 10 and 60 Mton equivalent TNT.

It is seen that the NO yields for 1, 10 and 60 Mton explosions are 0.49, 5.4 and  $35.5 \times 10^{10}$  g respectively. The yield in the range 1 to 10 Mton is about linear, with  $5 \times 10^9$  g of NO being



**Fig. 2** Nitric oxide concentrations as a function of time for a 10 Mton explosion. *a*, Shell (4), shock starts 155 ms after ignition; *b*, shell (5), shock starts 197 ms after ignition; *c*, shell (6), shock starts 273 ms after ignition. The pressure and temperature histories are also plotted. —, Temperature; ---, pressure; ···, [NO]/[M].

produced per Mton of explosive energy. This linearity breaks down somewhat for the 60 Mton explosion because in the outermost of the shells producing significant amounts of NO (shell (6)), the NO production is slow enough to be dependent on the time spent at high temperatures, rather than the cooling rate as is the case for the inner shells. Sixty megatons is about the size of the largest individual nuclear explosion ever made, in Russia in 1962.

The deduced production of  $5 \times 10^9$  g per Mton of explosive power can be compared with the findings of three previous studies.

The first by Davies<sup>17</sup> was primarily concerned with the chemical composition of the air in the shock wave and how the resulting changes in  $\gamma$  would affect the shock propagation. He did, however, conclude on the basis of a statistical mechanical treatment of equilibrium constants that at 4,000 K 4.6% of nitric oxide would be present. He also concluded that no NO would be produced at temperatures of 3,000 K or lower; that is because the statistical mechanical approach does not allow for the changes in the chemical reaction rates with temperature being slower than the rate of change of temperature. The amount of NO left after the passage of the shock wave was not of concern in this study.

**Table 2** Calculated NO Production

Explosion strength (Mton)	Shell No.	Air mass in shell ( $10^{12}$ g)	[NO]/[M]	[NO] ( $10^{10}$ g)	[NO] ( $10^{32}$ molecules)
1	4	0.075	0.017	0.13	0.26
	5	0.145	0.016	0.23	0.46
	6	0.270	0.005	0.13	0.26
			Total	0.49	0.98
10	4	0.75	0.015	1.2	2.4
	5	1.45	0.014	2.1	4.2
	6	2.70	0.008	2.1	4.2
			Total	5.4	10.8
60	4	4.5	0.015	6.8	13.6
	5	8.7	0.013	11.1	22.2
	6	16.4	0.011	17.6	35.2
			Total	35.5	71.0

In the second, Zel'dovich and Raizer<sup>18</sup> assume that all the air that had been taken to temperatures greater than 2,300 K in the shock wave would ultimately have equilibrium NO concentrations frozen at values characteristic of 2,300 K when returned to ambient temperatures. On this basis they concluded that a 20 kton equivalent TNT explosion would yield a concentration of NO of about 1%, equivalent to about 50 ton. On a linear extrapolation this means that a 1 Mton explosion would yield  $2.5 \times 10^9$  g. This is about half the yield indicated by the more comprehensive calculations outlined here. In the third study, Foley and Ruderman<sup>19</sup>, simply took one-third of the liberated explosive energy yield as remaining as thermal energy in the buoyant hot air and assumed that this energy would be used in heating a mass of air to 2,000 K. The physical basis of this assumption is not readily apparent from detailed studies of Taylor<sup>7</sup> and Brode<sup>20</sup>. They further assumed that all this air instantaneously produced a concentration of 0.8% NO. The time scale for NO production for curve (6) of Fig. 2 of this article demonstrates one limitation of this approach. However, this simplified treatment of the physics and chemistry of nuclear explosions yielded a similar result ( $10^{10}$  g of NO per Mton explosive energy), higher than that of our method by a factor of two.

What are the limitations of the treatment presented here? In arriving at the nitric oxide production rate, the inner three shells, denoted in Fig. 1, and containing 0.33, 3.3 and  $20 \times 10^{12}$  g, respectively, for 1, 10 and 60 Mton events have not been included. This is not only because of the inapplic-

ability of the Taylor formulations to these inner regions where radiative transfer may be relatively important but it might also be argued that these high temperatures gases absorb the ionizing radiations from the innermost region, so shielding the nitric oxide in the outer shells (4), (5) and (6). The chemistry of a hot ionized air mass, subjected to radioactive emissions, is not easily modelled. Any nitric oxide production in these innermost shells will be additional to  $5 \times 10^9$  g per Mton deduced from the outer shells. Also, all the calculations apply to a spherical shock wave. For explosions on or near the ground some of the energy would be absorbed in the Earth rather than propagated in the atmosphere, leading to a somewhat smaller nitric oxide production.

As mentioned earlier, a value of 1.4 for  $\gamma$ , the ratio of specific heats, was used in calculating the pressure-temperature histories of the shock wave. To test the effect of decreasing  $\gamma$ , the pressure-temperature histories were recalculated for a 10 Mton event using  $\gamma=1.3$ . The nitric oxide production was now attributed to shells (3), (4) and (5) rather than (4), (5) and (6). It was found that the total nitric oxide production was decreased to  $4.5 \times 10^9$  g per Mton.

The overall calculated NO production for an explosion was found not to be very sensitive to variation to any one of the rate coefficients  $k_3, k_4, k_{12}, k_{13}, k_{14}, k_{19}$  and  $k_{20}$  within their experimental limits. But simultaneously setting the first six of these ( $k_3$  to  $k_{15}$ ) to their lower limits and the other two ( $k_{19}$  and  $k_{20}$ ) to their upper limits reduced total nitric oxide production to  $2.7 \times 10^9$  g per Mton. Inspection of the course of the integrations showed that reactions (3), (12) and (14) were the chief producers of nitric oxide and reaction (19) was the principal destroyer. This is in agreement with the experimental observations of Camac and Feinberg. Thus the value of  $2.7 \times 10^9$  g per Mton is a lower limit in the light of current knowledge of rate coefficients.

The amounts of  $\text{NO}_2$  and  $\text{O}_3$  generated by explosions also formed part of the solutions of the differential equations. It was found that  $\text{NO}_2$  was always less than 1% of the nitric oxide production and that the  $\text{O}_3$  production was negligible. The fact that the  $\text{NO}_2$  amounts were so small provides some justification for omitting the higher oxides of nitrogen ( $\text{NO}_3, \text{N}_2\text{O}_3$ ). In these calculations, the temperature history below 1,500 K was not considered. Needless to say there will be considerable conversion of NO to  $\text{NO}_2$  as the air mass cools to ambient. This would account for the observations<sup>22</sup> of an orange colour to the nuclear cloud at high altitudes.

The chemical model outlined here is strictly speaking applicable only to dry air. In the real atmosphere, it is possible that a number of reactions involving water and its dissociation products should be incorporated. It is difficult to visualize a chemical mechanism at the relevant elevated temperatures by which water or its dissociation products at atmospheric mixing ratios could prevent the formation of NO. Species such as HNO,  $\text{HNO}_2$ ,  $\text{HNO}_3$  have dissociation energies less than  $\text{NO}_2$ , thus in the absence of some catalytic destruction of NO or  $\text{NO}_2$  by H, OH,  $\text{HO}_2$  and  $\text{H}_2\text{O}$  processes such as



cannot prevent the formation of NO in the shocked air masses. Further calculations on this point are in progress, but it is a fact that in the emissions of jet engines the gases contain high amounts of water and dissociation products and this does not apparently inhibit production of NO.

## Nitrogen Oxide Production by Concorde

The recommended value<sup>21</sup> for the emission of nitrogen oxides from the Concorde's Olympus Mark 602 engines is 13.8 g of NO per kg of fuel consumed, which is rather larger than

estimates based on measurements made at the National Gas Turbine Establishment, Pyestock. At a cruise altitude of about 55,000 foot, the engine's fuel consumption is about 4,550 kg h<sup>-1</sup> per engine. Thus assuming a trans-Atlantic crossing requires 2½ h flying time in the stratosphere, the total nitrogen oxide production per flight expressed in terms of NO is 670 kg. Thus one Concorde crossing the Atlantic, four times a day each day of the year produces 9.8 × 10<sup>5</sup> kg yr<sup>-1</sup> of NO.

Table 3 gives a year by year summation of all nuclear explosions<sup>19,22-24</sup> greater than 20 kton TNT together with the associated NO production deduced from the calculated yield of 5 × 10<sup>9</sup> g per Mton. In the fourth column is the number of Concordes that would have to fly across the Atlantic four times a day each day of the year to produce the same amount of NO as that year's nuclear weapon testing.

It is seen that the nuclear testing is equivalent during the period 1952 to 1958 to more than 100 fully operational Concordes. During 1961 and 1962, as many as 800 Concordes would have had to have been fully operational throughout the two years for the same gross NO injection. The assumption is made that all nitrogen oxides produced in explosions are ultimately transported into the stratosphere. As the greater proportion of radioactive debris in an air burst of 1 Mton or greater is injected into the stratosphere<sup>25</sup>, it is not unreasonable to assume that all nitrogen oxides will reach the stratosphere in a similar manner. Although Table 3 gives a summation of nuclear explosions greater than 20 kton TNT, the total yield of explosions between 20 kton, which probably do not inject material into the stratosphere<sup>25</sup>, and 1 Mton, which probably do, is only a small proportion of the total. The inclusion of these low yield explosions will make no significant differences to the estimates of the stratospheric injection of nitrogen oxides.

**Table 3** Calculated Annual NO Production from all Nuclear Tests greater than 20 kton and the Equivalent Number of Fully Operational Concordes

Year	Mton TNT	NO production 10 <sup>7</sup> kg	Equivalent No. of fully operational Concordes
1952	11.1	5.5	54
1953	0	0	0
1954	48.5	24.2	237
1955	2.0	1.0	10
1956	26.0	13.0	127
1957	13.5	6.7	66
1958	61.9	30.9	303
1959	0	0	0
1960	0	0	0
1961	120.6	60.3	591
1962	213.5	106.7	1,047
1963	0	0	0
1964	0	0	0
1965	0	0	0
1966	1.4	0.7	7
1967	3.5	1.7	17
1968	7.6	3.8	37
1969	3.0	1.5	15
1970	6.1	3.0	30
1971	1.6	0.8	8
1972	0	0	0

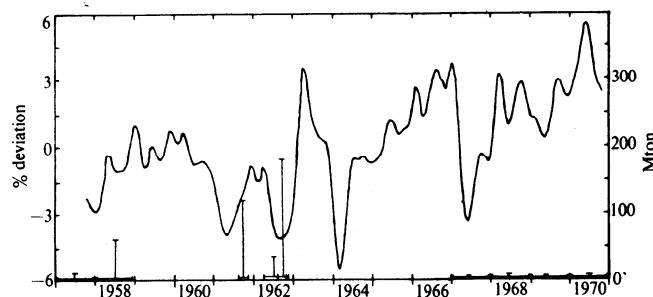
There will, however, be obvious differences between the stratospheric distribution due to aircraft emissions and that due to more rapid injections by explosions. In the first place, the aircraft injections are confined to the limited region of air routes, and operational flight altitudes in the lower stratosphere. The nuclear injections cover a much wider altitude range, depending on the strength of the explosion; the cloud of debris from a 1 Mton event typically stabilizes<sup>25</sup> at a height of about 22 km whereas that of a 10 Mton event would

reach about 32 km. Thus the Concorde emissions at the operational height of 17 km are always below the maximum in the vertical ozone profile, while the nitrogen oxides from nuclear explosions could well stabilize in the same height range as the ozone maximum.

It must therefore be accepted that amounts of NO at least comparable with those expected from large fleets of Concorde aircraft have already been directly injected into the stratosphere. If the atmospheric ozone budget is sensitive to injections of anthropogenic nitrogen oxides then one would expect the effects of the nuclear testing programme to be reflected in the past records of total ozone amounts. This applies especially to 1961 and 1962.

## Ozone Records

The total amount of ozone in the atmosphere above any point on the Earth's surface is highly variable, with large fluctuations from day to day and with a well established annual cycle which has a maximum in the early spring and a minimum in the late autumn. If the nitrogen oxides from the testing of nuclear weapons have affected total amounts of ozone, then one would expect this to be reflected in the ozone records since 1952, with special emphasis on the years 1961 and 1962 when weapons yielding 334 Mton were exploded, more than half the total explosive energy of all tests. Those tests before 1952



**Fig. 3** Smoothed deviations from monthly means of total ozone from seventeen stations in the period 1957 to 1970 and the intensity and timetable of nuclear explosions in this period. —, Deviation; ⊥, nuclear events.

were all of less than 1 Mton yield and contributed little to the total stratospheric injections.

In Fig. 3 are plotted ozone data from the seventeen stations in the northern hemisphere with the longest continuous record (see Table 4). The deviation from the monthly mean, expressed as percentage of that mean, is plotted monthly as a function of time. In this way the annual and short term fluctuations are removed. Also the mean of the seventeen stations was subjected to conventional five term binomial smoothing.

The stations were selected on the following criteria. The records exist from 1957 or 1958, the beginning of the IGY period, when many more stations commenced operation, they do not have gaps of more than 18 consecutive months in their data; and they have more than 110 monthly mean values for the total period 1957 to 1970. Stations making measurements with the Russian filter ozonometer were excluded because it has been demonstrated<sup>26</sup> that results from these instruments differ significantly from those of the Dobson ozone spectrophotometer for solar zenith angles greater than 60° or in the presence of haze. This may be important on account of

secular changes in haze (R. N. Kulkarni, private communication). Furthermore only ozone measurements in the northern hemisphere are considered because most nuclear weapon debris has been injected there. In any case very few stations in the southern hemisphere would have met the criteria of long term continuity. The periods of weapon testing together with total megaton yield for each of nine periods are also indicated on Fig. 3. The American equatorial and Russian high latitude tests of 1961–62, are separated on Fig. 3, with the American tests coming between the two periods of Russian tests.

It might be expected that if nitrogen oxides from the nuclear explosions are to modify the total ozone amount, then this would be reflected in the records, covering the northern

**Table 4.** Ozone Records of the Stations Used in Fig. 3

Station	No. of months	Mean total ozone	Slope (% per decade)	Error of slope ( $\sigma$ )
Arosa (47° N 10° E)	158	334	1.2	0.9
Cagliari Elmas (39° N 9° E)	161	329	8.6	0.9
Camborne (50° N 5° W)	115	338	6.3	1.7
Edmonton (54° N 114° W)	162	357	2.9	1.0
Kagoshima (32° N 131° E)	151	289	1.9	1.2
Kodaikanal (10° W 77° E)	161	255	10.6	0.5
Lerwick (60° N 1° W)	151	348	7.2	1.2
Messina (38° N 16° E)	141	346	3.5	0.9
Napoli (41° N 14° E)	137	301	-1.3	1.1
New Delhi (29° N 77° E)	159	270	7.8	1.1
Oxford (52° N 1° W)	162	353	4.3	1.0
Resolute (75° N 95° W)	143	390	3.6	1.8
Reykjavik (64° N 22° W)	134	339	-1.7	1.9
Sapporo (43° N 141° E)	155	371	1.0	0.8
Tateno (36° N 140° E)	160	325	0.0	0.9
Tromsø (70° N 19° E)	121	331	0.6	2.0
Vigna Di Valle (42° N 12° E)	162	341	1.1	0.9
Mean of stations	162	330	6.3	1.7

hemisphere, delayed by a period dependent on stratospheric mixing times and relevant chemical reaction rates. It seems to us that these records do not provide evidence for such a modification.

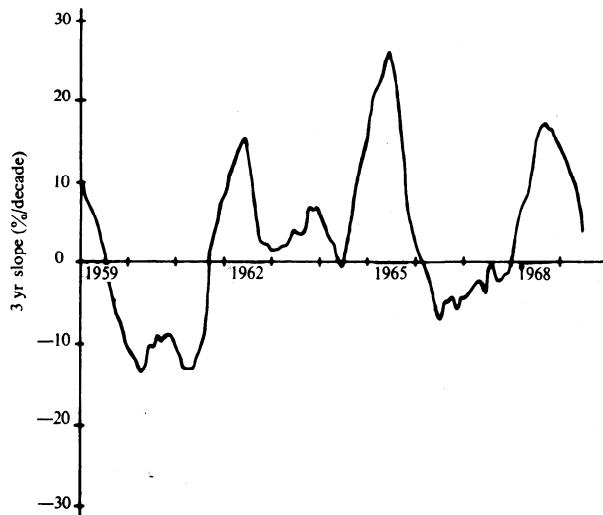
It has, however, been suggested by Johnston *et al.*<sup>27</sup> on the basis of an analysis of the records of ozone measuring stations from 1960, including those in the Soviet Union and some in the southern hemisphere, that in the northern hemisphere there was a significant decrease (-7.6% per decade) in ozone during 1960–62, followed by an increase (+5.6% per decade) in 1963–70. Johnston *et al.* argue on the basis of these figures, that "the oxides of nitrogen from nuclear bomb tests of 1952–62 constituted a measurable injection and the consequent reductions of ozone may be ascribable (perhaps only in part) to this injection experiment". They also speculate that the ozone increase in 1963–70 may represent a recovery from the effects of the test period.

The ozone data going back to late 1957 given in Fig. 3, do not support the contention that the period 1960–62 is of any particular significance with respect to the periods of nuclear testing. Moreover there is considerable danger in comparing ozone trends over an interval of 3 yr. This is demonstrated in Fig. 4 in which the 3 yr slopes of the seventeen station ozone records are plotted monthly. It is seen that the slopes vary between about +26% and -13% per decade and so there is no significance to the -7.6% per decade obtained by Johnston for 1960–62. Indeed during 1963–70, there was a period when the 3 yr slope was also negative.

The upwards tendency of the trace of Fig. 3 since 1961 agrees with the findings of Komhyr *et al.*<sup>28</sup> that there has been an increase of total ozone of up to 10% at a number of stations during the past decade (1961–70).

There have been a number of other studies of trends of ozone based on much longer records of data. Notably Willett<sup>29</sup> and Christie<sup>30</sup>, both on the basis of records going back to 1933,

detected a negative and largely unexplained correlation of total ozone with sunspot number. The ozone minimum precedes the sunspot maximum by about 20 months. London and Oltmans<sup>31</sup> were, however, unable to find such a correlation in the Arosa and Tromsø records, which formed the bulk of the Willett, Christie data before 1945. Paetzold *et al.*<sup>32</sup>, on the evidence of direct balloon-borne optical ozone soundings over central Europe between the years 1951 to 1972, report a positive correlation between sunspot number and the ozone amounts between 20 and 30 km. The evidence for this corre-



**Fig. 4** Percentage increase expressed in % per decade for the total ozone calculated from the deviations of the monthly means for seventeen stations over 3 yr intervals from 1959 to 1969.

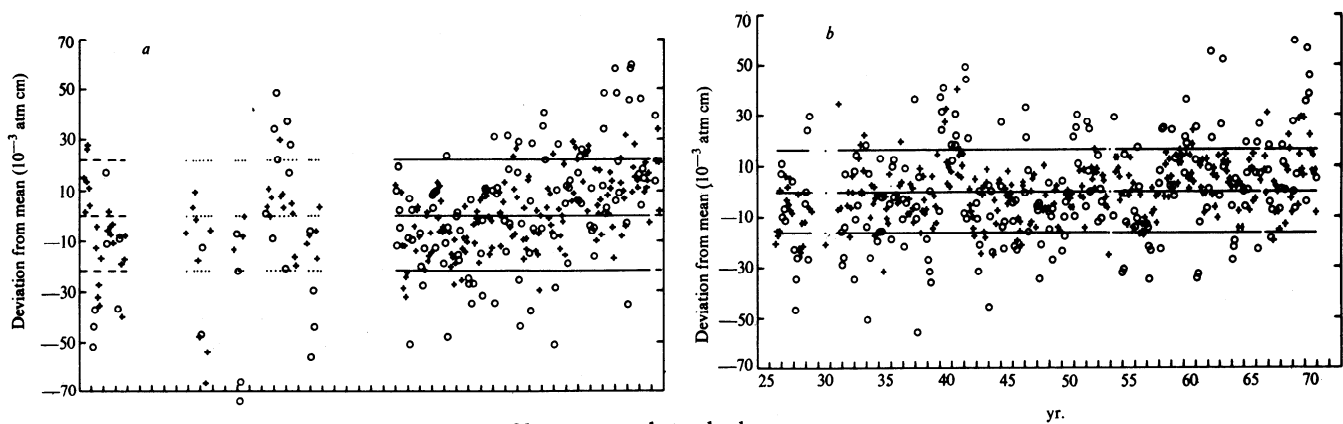
lation is, however, not conclusive because of the lack of data in the first half of the period.

There are only two ozone observing stations with reasonably complete long term records. These are Arosa and to a lesser degree Oxford, both from 1926. In Fig. 5 the deviation from the monthly mean is shown for both these stations. The Oxford data between 1933 and 1944 have not previously been published, those for Arosa are given by Perl and Dütsch<sup>33</sup>.

These long term records demonstrate the high variability in total ozone over a wide variety of time scales and indicate the difficulty in detecting any short term trends. In common with other data presented here, there is nothing to suggest that nitrogen oxides from the testing of nuclear weapons in the atmosphere have had any effect on the total ozone.

## Implications

In this article the production of nitrogen oxides in the shock wave of explosions associated with the testing of nuclear weapons in the atmosphere has been calculated. This has allowed the total injection of nitrogen oxides into the stratosphere to be deduced for each year in which nuclear tests have taken place. These amounts have been compared with those expected from the engine exhaust products of fleets of Concorde each flying in the stratosphere for more than 10 h every day of the year. We conclude that past nuclear explosions have been equivalent, as far as nitrogen oxide stratospheric injections are concerned, to large numbers of these fully operational Con-



	N yr mean and standard error												Mean
	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	
<b>Oxford</b>													
Mean	348	384	391	395	388	371	350	336	308	294	291	310	348
s.e.	29	33	29	26	18	14	19	13	23	19	19	17	22
N	26	24	30	31	28	31	33	26	32	33	23	25	342
<b>Arosa</b>													
Mean	336	361	370	371	361	340	322	308	289	280	283	307	327
s.e.	21	26	24	19	14	12	10	11	12	11	12	15	16
N	41	41	42	42	42	40	41	44	43	41	43	42	502

Fig. 5 Deviation of monthly total ozone from the mean of that month for Oxford, 52° N 1° W (a), and Arosa, 47° N 10° E (b), from 1925 to 1971. ○, Values for January to March inclusive, when the total ozone is at its most variable; +, values for all other months. The units represent the equivalent thickness of ozone at standard temperature and pressure.

cordes. For instance, during the years of maximum nuclear activity, 1961 and 1962, the number of Concordes giving equivalent nitrogen oxide emissions would have been about 600 and 1,000 respectively. Analysis of the ozone records reveal no detectable changes in the total atmospheric ozone during and after the periods of nuclear weapon testing. Although the two modes of nitrogen oxide injection may not be identical from the meteorological view point, the conclusion that massive injections of nitrogen oxides into the stratosphere do not upset the ozone layer seems inescapable. Such a conclusion has profound implications for our understanding of

the photochemical processes in the stratosphere, as it is only by postulating an ozone sink due to natural nitrogen oxide at the level of 1 to 10 parts per 10<sup>9</sup> that current theories are able to account for the natural concentrations of ozone in the stratosphere. It may be that other factors such as solar radiation, stratospheric circulation, refinement of chemical rate coefficients and hitherto unconsidered chemical sinks may all play a part in bringing theory closer to measurement.

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