

Chapter 8

Nitrogen Oxides: Vehicle Emissions and Atmospheric Chemistry

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Abstract An overview of vehicle emissions, ambient concentrations, and atmospheric chemistry of NO, NO₂, and N₂O is presented. We start with a discussion of air quality standards and trends in NO₂ levels. We then discuss the formation of nitrogen oxides in vehicle engines, technologies used to control emissions of nitrogen oxides, and the trends in vehicle emissions.

Keywords Nitrogen oxides • NO • NO₂ • Vehicles • Air pollution

8.1 Introduction

It is well recognized that emissions from vehicles can play an important role in the degradation of local air quality and contribute to radiative forcing of climate change. There are three different classes of vehicle emissions which contribute to local air pollution; hydrocarbons, nitrogen oxides, and particulate matter. The goal of the present paper is to provide an overview of the emissions of nitrogen oxides from vehicles and their atmospheric chemistry. There are three nitrogen oxides that are emitted from vehicles; NO, NO₂, and N₂O. Nitrogen monoxide (NO) and nitrogen dioxide (NO₂) are interconverted rapidly (typically on a time scale of minutes) in atmospheric processes and their chemistry is so interlinked that they are usually referred to together as NO_x (NO + NO₂). NO_x chemistry plays an important

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role in the formation of local air pollution (smog). In stark contrast to NO_x , dinitrogen monoxide (N_2O) is inert to chemical and physical processes in the lower atmosphere, has an atmospheric lifetime of 114 years [19], and plays no role in local air quality. N_2O is a potent greenhouse gas although as we discuss in the present article the emissions from vehicles are small and only make a small contribution to radiative forcing of climate change.

The goal of the present paper is to provide an overview of nitrogen oxide emissions from vehicles and their atmospheric chemistry. We start with a discussion of air quality standards and trends in NO_2 levels. We then discuss the formation of nitrogen oxides in vehicle engines, technologies used to control emissions of nitrogen oxides, and the chemistry of nitrogen oxides after they have been emitted into the atmosphere. We highlight areas of current research interest and future research directions.

8.2 Air Quality Standards

Under the Clean Air Act the United States Environmental Protection Agency (USEPA) establishes air quality standards to protect public health and the environment [28]. USEPA has set national air quality standards for six common air pollutants. These are carbon monoxide, ozone, lead, particulate matter, sulfur dioxide, and nitrogen dioxide. Using a nationwide network of monitoring sites, EPA has reported ambient air quality trends for nitrogen dioxide (NO_2). Figure 8.1 shows the average annual NO_2 concentration measured in 81 monitoring sites across the U.S. As seen from Fig. 8.1, there has been a significant and steady trend

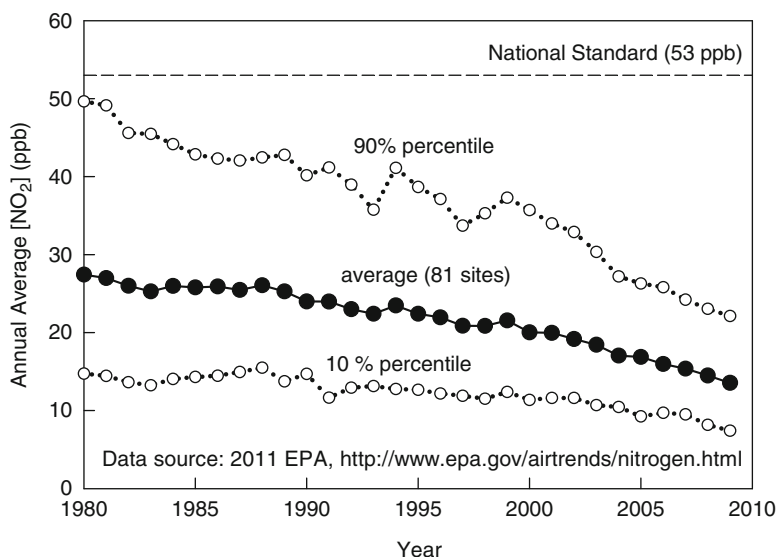


Fig. 8.1 Annual average NO_2 concentrations from 81 sites in the U.S. (average, 90th, and 10th percentile) (Data from USEPA [28])

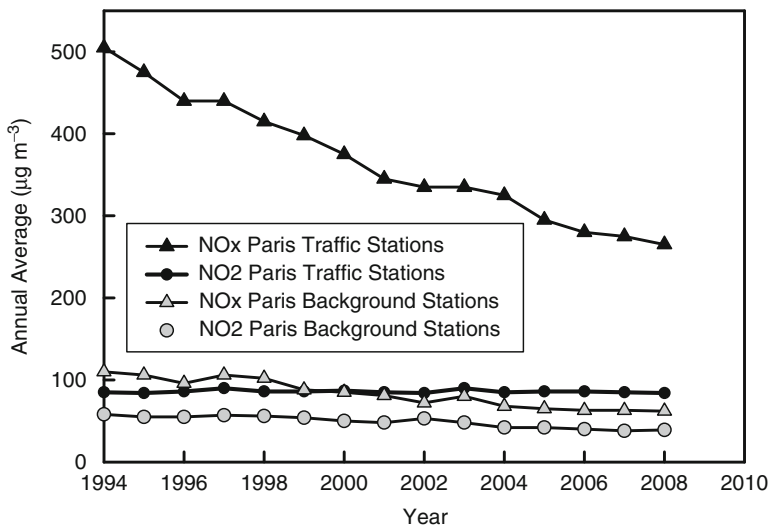


Fig. 8.2 Annual average NO_x (triangles) and NO₂ (circles) concentrations from traffic (filled symbols) and background (grey symbols) stations in Paris (Data were taken from Carslaw et al. [10])

of decreased NO₂ levels in air in the U.S. over the past 30 years. This trend reflects the success of emission control measures on mobile and stationary sources adopted since the enactment of the Clean Air Act in 1970.

USEPA set the annual average NO₂ standard of 53 ppb (102 µg/m³) in 1971. USEPA reviewed the NO₂ standard in 1985 and 1996 and decided to retain the 53 ppb annual average standard. In 2010 EPA established a new 1-h NO₂ standard at 100 ppb (192 µg/m³) and decided to retain the 53 ppb annual average standard. As seen from Fig. 8.1, the levels of NO₂ in air in the U.S. are typically substantially below the annual average standard.

The European Commission set a 1 h NO₂ limit value of 200 µg/m³ (104 ppb) and http://ppdys1138/eHR-ESS/Login_Page.aspx annual NO₂ limit value of 40 µg/m³ (21 ppb) effective in 2010. In China the 1 h NO₂ limit value is 240 µg/m³ (125 ppb), daily NO₂ limit value is 120 µg/m³ (63 ppb), and annual NO₂ limit value is 80 µg/m³ (42 ppb) for cities. NO_x concentrations in European cities have declining significantly over the past few decades mainly as a result of reduced traffic emissions, however NO₂ concentrations in European cities over the past decade are declining slowly, or are showing little trend [10]. Figure 8.2 shows the trend in annual average concentrations of NO_x and NO₂ reported by Carslaw et al. [10] from stations in Paris which are close to traffic emissions and stations which are located in what are considered urban background locations somewhat removed from the influence of direct emissions. The slower decrease in NO₂ concentrations than NO_x concentrations in Europe has been attributed to decreased overall NO_x levels in vehicle exhaust with a higher fraction of NO₂ within the exhaust [10]. The annual average NO₂ limit value in Europe of 40 µg/m³ (21 ppb) effective in 2010 is approximately a factor of 2.5 times lower, and more difficult to achieve, than the US annual average NO₂ standard of 53 ppb.

8.3 Nitrogen Oxide Emissions from Vehicles

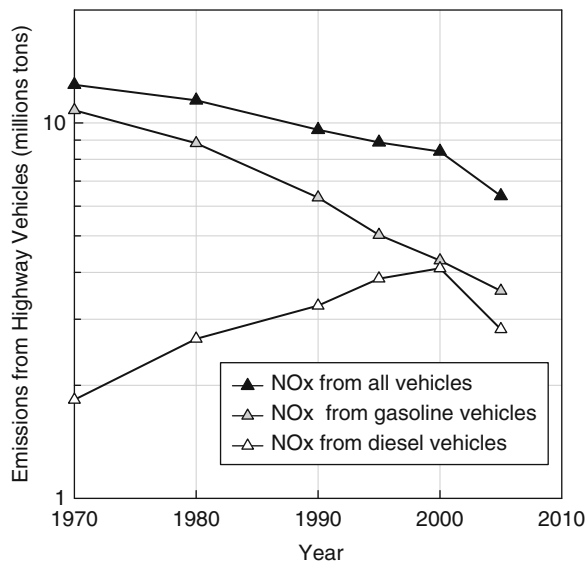
NO_x emissions from vehicles can be traced to oxidation of fuel-bound nitrogen and high temperature oxidation of atmospheric nitrogen in the combustion chamber [13, 18]. The chemistry associated with NO_x formation and treatment in vehicles has been discussed by Wallington et al. [30]. The vast majority of NO_x emissions come from oxidation of atmospheric nitrogen initiated via reaction with O atoms, $\text{O} + \text{N}_2 = \text{NO} + \text{N}$, followed by $\text{N} + \text{O}_2 = \text{NO} + \text{O}$, and $\text{N} + \text{HO} = \text{NO} + \text{H}$ [17]. This is known as the Zeldovich mechanism after its discoverer [34]. Oxygen atoms are produced by the unimolecular thermal decomposition of molecular oxygen, hence the formation of NO increases sharply with temperature.

There are two methods to reduce the emission of NO_x from vehicles. First, the engine design and operation can be chosen to minimize the formation of NO_x . Second, once formed the NO_x can be treated (reduced to N_2) in the exhaust system before leaving the tailpipe. Both approaches are used in modern engines. Reducing the burned gas temperature is an effective means to limit NO_x formation within the engine. One commonly employed strategy, termed exhaust gas recirculation (EGR), involves recirculating a fraction (5–10%) of the exhaust gas to the intake manifold. The dilution effect combined with replacement of air with the exhaust gases CO_2 and H_2O , which have higher heat capacities, leads to lower combustion temperatures and hence reduced NO formation.

Exhaust catalysts are highly effective devices used to reduce the engine-out hydrocarbon, CO, and NO_x emissions [14, 15, 20, 30]. Automotive catalytic converters on gasoline vehicles typically consist of one or more ceramic monolithic honeycomb substrates wrapped with a mounting material and contained in a metal can. The monolith surface is coated with alumina, other high surface area oxides such as ceria or zirconia, and precious metals such as Pt, Rh, and Pd. The precious metals provide catalytic reduction/oxidation of the pollutants in the exhaust gas, while the oxides can improve catalytic efficiency by storing and giving up oxygen as engine operating conditions change. These catalysts are very efficient after the catalyst has reached its optimum operating temperature (light-off). Oxidation catalysts were introduced in the mid-1970s to control HC and CO emissions. When more stringent NO_x control was mandated, a new type of catalyst was required that could oxidize CO and HC to CO_2 and H_2O while simultaneously reducing NO_x to N_2 and O_2 . This type of catalyst is often called a “three-way” catalyst because it decreases the emissions of three important compounds, or classes of compounds: CO, HC, and NO_x . To meet the requirement of simultaneously oxidizing CO and HC while reducing NO_x , the engine must be operated at close to the stoichiometric air/fuel (A/F) ratio, requiring careful feedback control using an on-board exhaust gas sensor. The overall conversion efficiency is improved somewhat by causing the A/F ratio to oscillate by ~2–3% around the stoichiometric A/F ratio.

The primary regulated emissions from diesel engines are similar to those from gasoline engines (e.g. organics, CO, and NO_x), but there are differences in degree. Exhaust CO and HC emissions are lower in diesel engines and can be converted to H_2O and CO_2 with an exhaust oxidation catalyst. Engine out NO_x levels are

Fig. 8.3 Emissions from U.S. highway diesel (*open symbols*), gasoline (*grey symbols*) vehicles, and all vehicles (*filled symbols*) (Data were taken from Davis et al. [12])



lower for diesel engines than their stoichiometric gasoline counterparts reflecting the somewhat lower combustion temperatures in the diesel engine. However, tailpipe-out NO_x emissions can be higher from diesels reflecting difficulties in reducing NO_x to N_2 in the highly oxidizing environment of diesel exhaust which typically contains approximately 14% O_2 .

Options for treating NO_x in diesel exhaust include Lean NO_x Traps (LNT) and urea Selective Catalytic Reduction (SCR). LNTs trap and store NO_x in the form of nitrates on a base metal. When the trap is full the NO_x is released during a rich transient and then reduced using a Pd/Rh catalyst. LNTs tend to use a large amount of expensive precious metals, although the overall content has decreased in recent years. In urea SCR systems an aqueous solution of urea is injected into the exhaust stream. Urea undergoes thermal decomposition to give NH_3 which is then used to selectively reduce NO_x [21]. For SCR systems, the urea dosing system adds some cost which is offset by the use of a base metal catalyst. Most manufacturers, especially for medium- and heavy-duty vehicles, have adopted SCR strategies for NO_x control. As a result of the adoption of emission control technologies the emissions of NO_x from highway vehicles in the U.S. is declining as shown in Fig. 8.3 [12, 32]. As the on-road vehicle fleet is replaced with vehicles equipped with modern emission control technologies, the progress indicated in Fig. 8.3 will continue and further reductions in NO_x emissions are expected over the coming decades. The progress made shown in Fig. 8.3 is even more impressive in light of the fact that the total vehicle miles travelled on U.S. highways increased by approximately a factor of 3 from 1970 to 2005 [12].

To estimate future emissions from road transportation the International Energy Agency (IEA) worked together with the World Business Council for Sustainable development (WBCSD) to develop a global transport spreadsheet model. The Sustainable Mobility Project (SMP) spreadsheet model is available from the WBCSD

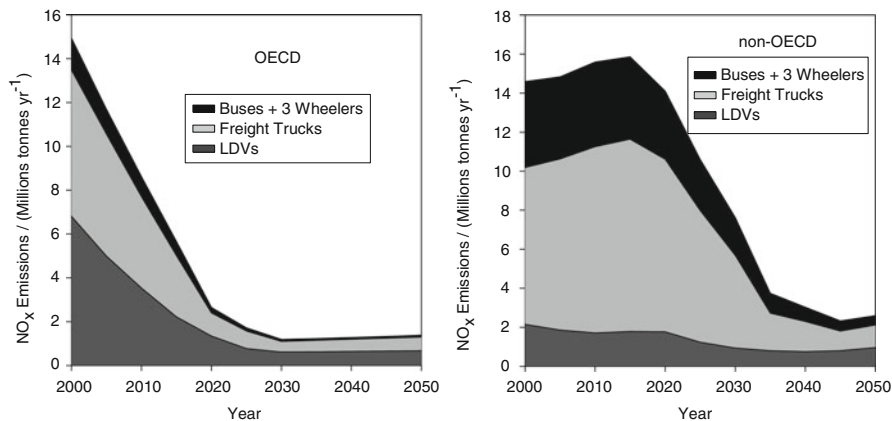


Fig. 8.4 Projected NO_x emissions from OECD (*left panel*) and non-OECD (*right panel*) countries in the SMP Reference Case [33]. The *bottom dark grey* section in *both panels* shows NO_x emissions from light-duty vehicles (passenger cars and trucks), the *middle light grey* section shows emissions from freight trucks and the *top black* section shows the combined emissions trends from buses and three wheelers (mopeds and motorcycles)

website (<http://www.wbcds.org>) and provides a tool for projecting emissions associated with global transportation over the time period 2000–2050. Many of the world’s leading automotive related companies were involved in developing the model: General Motors Corporation, Toyota Motor Corporation, Ford Motor Company, DaimlerChrysler AG, Honda Motor Company, Volkswagen AG, Nissan Motor Company, Renault SA, BP plc, Royal Dutch/Shell Group of Companies, Michelin, and Norsk Hydro ASA [33]. The reference case SMP model presents one possible set of future conditions, based on existing trends and including existing policies, population projections, income projections and expected availability of new technologies. In general, no major new policies are assumed to be implemented beyond those already implemented in 2003.

An exception was when there was clear evidence of “policy trajectories” such as future policy actions that are either explicit or implicit in other trends. For example, a clear trend was discernable in the developing world to adopt vehicle emissions standards similar to those already implemented in more developed nations. Figure 8.4 shows the projected decrease in NO_x emissions in the SMP model. The left panel gives the emissions from Organization of Economic Cooperation and Development, OECD, countries (Australia, Austria, Belgium, Canada, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Mexico, The Netherlands, Norway, Japan, Korea, New Zealand, Poland, Portugal, Slovak Republic Sweden, Switzerland, United Kingdom, USA). The right panel gives the projected emissions from non-OECD countries. As shown in Fig. 8.4, substantial reductions in the emissions of NO_x are anticipated from the on-road global vehicle fleet over the coming decades. The projected decreases reflect the diffusion of modern emission control technology into the on-road fleet (approximately 10–15 year time lag) and comes despite a factor of approximately 2 projected increase in mobility delivered by light duty vehicles (1.5×10^{13} passenger km in 2000, 3.5×10^{13} passenger km in 2050) [33].

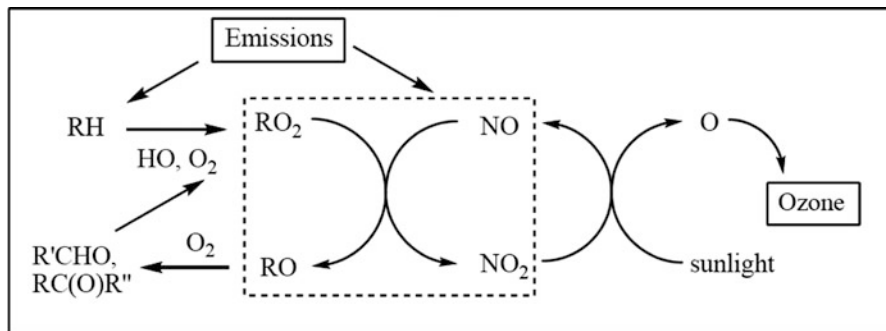


Fig. 8.5 Simplified mechanism for photochemical production of ozone illustrating the central importance of the $\text{RO}_2 + \text{NO}$ reaction (*dashed box*)

In the process of reducing NO_x to N_2 in exhaust catalysts some N_2O is formed and escapes through the tailpipe. While N_2O is a potent greenhouse gas, its emission from vehicles is modest and it has a global warming impact which is only approximately 1–3% of that of CO_2 emitted from the on-road vehicle fleet [31].

8.4 Atmospheric Chemistry of Nitrogen Oxides

Nitrogen oxides play a central role in the reactions that lead to the photochemical formation of ozone in the lower atmosphere associated with urban air pollution. The chemistry is represented in a very simplified form in Fig. 8.5.

The chemistry is initiated by reaction of HO radicals with hydrocarbons (RH) to give alkyl radicals (R) which, in one atmosphere of air, add O_2 rapidly (within 10^{-7} s) to give peroxy radicals, RO_2 . The dominant fate of RO_2 radicals in urban air is reaction with NO which occurs with a rate constant of the order of $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [3, 4] under ambient conditions (see Fig. 8.6). Typical NO levels in polluted urban air are 10–100 ppb and thus the lifetime of RO_2 radicals is approximately 0.1–1.0 s. Alkoxy radicals, RO, have an atmospheric lifetime typically of the order of 0.01–0.10 ms and undergo isomerization, decomposition via C–C bond scission, or reaction with O_2 to give carbonyl containing compounds which in turn can react with HO radicals to generate more peroxy radicals. The reaction of RO_2 (and HO_2 generated in the $\text{RO} + \text{O}_2$ reaction) with NO generates NO_2 which is a brown colored gas and absorbs at 400–450 nm. Photolysis of NO_2 gives O atoms and regenerates NO which reacts with more RO_2 radicals to form more NO_2 . The NO_2 photolysis rate, J_{NO_2} , in the lower atmosphere (troposphere) depends on the cloud cover and is typically in the range $(0.3\text{--}1) \times 10^{-2} \text{ s}^{-1}$, giving a lifetime of NO_2 of several minutes. In one atmosphere of air, O atoms add O_2 with an effective bimolecular rate constant of $1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $[\text{O}_2] = 5.2 \times 10^{18} \text{ cm}^{-3}$, and O atoms have a lifetime of 13 μs with respect to conversion into ozone.

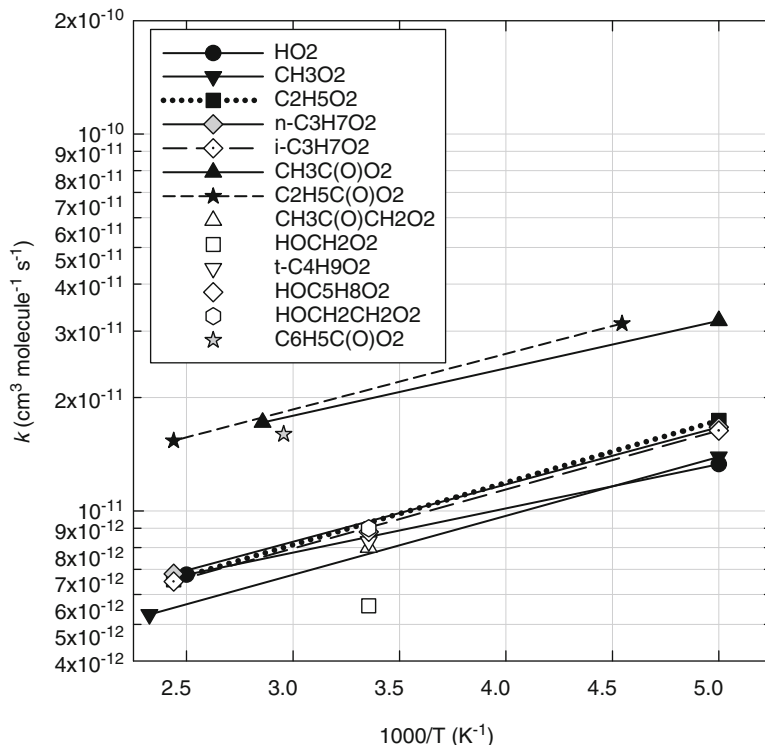


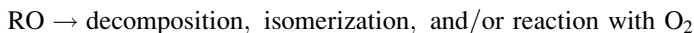
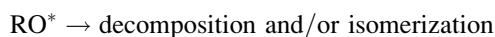
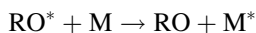
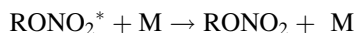
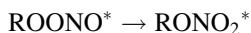
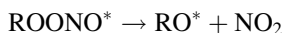
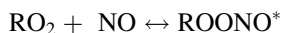
Fig. 8.6 Rate coefficients for reactions of selected peroxy (RO_2) and acyl peroxy ($\text{RC}(\text{O})\text{O}_2$) radicals with NO recommended by IUPAC [3, 4]

Figure 8.5 does not include the processes that limit ozone formation, such as the formation of nitric acid and organic nitrates (RONO_2). The addition reaction of HO radicals with NO_2 gives HNO_3 . Nitric acid does not participate in gas phase ozone forming reactions and is removed by wet and dry deposition. Formation of HNO_3 is a major loss mechanism for atmospheric NO_x and limits the formation of ozone. Organic nitrates, RONO_2 , are formed as minor, but important products, in the reaction of RO_2 radicals with NO.

Acyl peroxy nitrates (e.g., $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) are formed via the association reaction of NO_2 and acyl peroxy radicals (e.g., $\text{CH}_3\text{C}(\text{O})\text{O}_2$). RONO_2 and $\text{RC}(\text{O})\text{OONO}_2$ species tend to be less reactive than their parent hydrocarbons and serve as sinks for radicals and NO_x in urban air. Acyl peroxy nitrates such as $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ commonly known as peroxyacetyl nitrate or PAN, $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OONO}_2$ commonly known as peroxy propionyl nitrate or PPN, and $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONO}_2$ commonly known as peroxy benzoyl nitrate or PBzN are powerful lacrymators and are responsible for the eye irritation associated with air pollution. Concentrations of PAN in urban air typically exceed those of PPN and PBzN by factors of approximately 10 and 100, respectively, reflecting the source strengths of the corresponding aldehyde precursors.

As illustrated in Fig. 8.5, the reaction of RO₂ radicals with NO plays a central role in tropospheric ozone formation. Recognition of the importance of this reaction has led to a large number of experimental and computational studies which have provided a wealth of information. Figure 8.6 shows Arrhenius plots of the rate coefficients for reactions of RO₂ radicals (including HO₂) with NO determined in experimental studies as recommended by IUPAC [3, 4]. The kinetics of the reactions of simple alkyl peroxy radicals (e.g., HO₂, CH₃O₂, C₂H₅O₂, C₃H₇O₂, CH₃C(O)O₂) with NO are well established [3, 4, 24, 27, 29]. At 298 K the reactions of alkyl peroxy radicals (CH₃O₂, C₂H₅O₂, C₃H₇O₂) and acylperoxy radicals (e.g., CH₃C(O)O₂, C₂H₅CO(O)₂) proceed with rate coefficients of approximately 1×10^{-11} and 2×10^{-11} cm³ molecule⁻¹ s⁻¹. The reactions display negative temperature dependencies (rates increase with decreasing temperature) indicating that the reactions proceed via a mechanism involving the formation of an adduct intermediate. The database for substituted peroxy radicals (e.g., oxygenated species such as HOCH₂O₂ and halogenated species such as CH₂ClO₂) is more limited and further work is needed to establish the kinetics of their reactions with NO.

Experimental and theoretical studies have shown that the RO₂ + NO reaction proceeds via a complicated mechanism which can be represented as:



The yield of organic nitrates increases with size of the RO₂ radical, increasing total pressure, and decreasing temperature. The nitrate yield can be substantial for large peroxy radicals (e.g., approximately 20–30% for C₈H₁₇O₂ and C₁₀H₂₁O₂ [1, 2]) but is low for small peroxy radicals (e.g., <0.5% for CH₃O₂ [27]) in 760 Torr of air at 298 K. Empirical expressions have been developed to estimate nitrate yields [1] but our fundamental understanding of nitrate formation is limited.

The RO₂ + NO reaction has a substantial exothermicity and chemical activation in the nascent RO^{*} atmospheric reactivity [23]. For chemical activation to be significant three conditions need to be satisfied: (i) the lifetime of ROONO^{*} must be long enough ($>10^{-12}$ s) to enable efficient intramolecular energy flow, but short enough ($<10^{-9}$ s) that collisions with the diluent gas do not remove a significant fraction of the ROONO^{*} excitation (ii) the RO radical must possess a

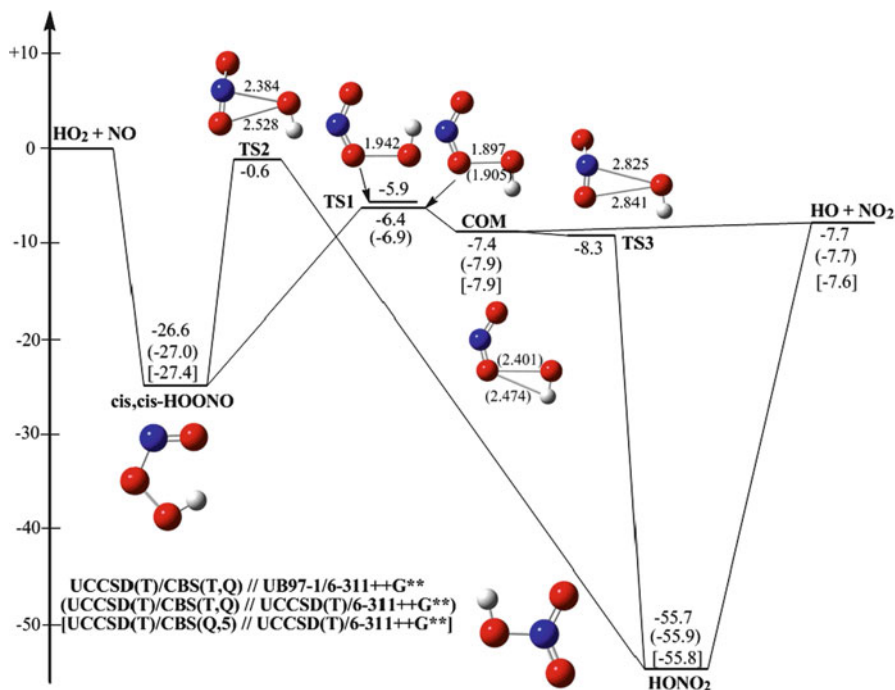


Fig. 8.7 Potential energy surface for the reactions initiated by $\text{HO}_2 + \text{NO}$ [6]. Optimized geometries and energies (including zero point energy) were obtained using the levels of theory shown as abbreviations (Energies are expressed in units of kcal mol^{-1} ; $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$)

decomposition, or isomerization, pathway which has an activation barrier which is comparable to, or lower than, the excitation of the nascent RO^* radical and (iii) the overall rate of prompt decomposition of RO^* must be sufficiently fast (i.e., the A factor for decomposition must be sufficiently large) that collisions with the diluent gas do not remove a significant fraction of the RO^* excitation prior to “prompt” decomposition.

Numerous theoretical treatments of the $\text{RO}_2 + \text{NO}$ reaction mechanism have been published. These include quantum chemical calculations [22, 26] of the structures and relative energies of the intermediates, as well as master equation [5, 16, 35, 36] and classical trajectory simulations [11, 25] of the chemical reactions. The $\text{ROONO}^* \rightarrow \text{RONO}_2$ isomerization step has posed particular theoretical challenges [9]. The general mechanism for the homologous $\text{RO}_2 + \text{NO}$ reactions is currently believed to be analogous to that for $\text{HO}_2 + \text{NO}$, which is illustrated in Fig. 8.7. The initial reaction produces vibrationally excited *cis,cis*-HOONO, which can rapidly re-dissociate or pass through transition structure TS1 on the way to forming $\text{HO} + \text{NO}_2$ or HONO_2 . The details of this process are not fully understood, because the quantum chemistry calculations for these species are very challenging. Moreover, dynamics calculations indicate that slow intramolecular vibrational energy redistribution may also play a role [25]. Transition structure TS2 is energetically accessible, but most of the reaction is believed to pass through TS1.

In calculations that are currently underway, high level quantum chemistry methods (i.e. UCCSD(T)/CBS(T,Q)//UB97-1/6-311++G**) generally support the calculations of Butovskaya et al., which were carried out at lower levels of theory [9]. The results suggest that after passing through TS1, the reaction encounters a very shallow well on the potential energy surface, where the reactive flux bifurcates: >99% of the reaction proceeds to form HO + NO₂, but a small fraction may instead proceed into the HONO₂ potential energy well, possibly explaining the reported experimental yields of HONO₂ [7–9]. Master equation simulations are being carried out to investigate these yields quantitatively [6]. Replacement of the H-atom by organic groups is expected to result in changes in relative energies, chemical lifetimes, and product branching ratios, as in previous studies.

8.5 Conclusions

While vehicles are a significant source of NO_x in urban areas, the emissions from vehicles are currently declining in the OECD countries and are expected to decline in non-OECD countries in the future (see Fig. 8.4). The decreased NO_x emissions from vehicles reflects improved emissions control technology in new vehicles and the replacement of older vehicles as they are retired from the on-road fleet. NO_x and NO₂ concentrations in U.S. cities have been declining over the past few decades. NO_x concentrations have been declining in European cities but there is little, or no, trend for NO₂ over the past decade. The reaction of peroxy radicals (RO₂) with NO plays a very important role in photochemical ozone production. As a result of a large number of experimental and computational studies the general features of the RO₂ + NO reactions are clear. For peroxy radicals derived from hydrocarbons: (i) kinetic data for reactions with NO appear to be indistinguishable, (ii) empirical methods to estimate nitrate yields are available, and (iii) chemical activation of RO radicals can be important. For peroxy radicals derived from oxygenated and halogenated organic compounds: (i) kinetic data for reactions with NO are scattered, (ii) nitrate yields appear to be very low and methods to estimate nitrate yields are not available, and (iii) chemical activation of RO radicals can be important. Further experimental work to better define the kinetics and nitrate yields in the reactions of peroxy radicals derived from oxygenated organics would be useful. Theoretical master equation calculations are currently being carried out on the HO₂ + NO reaction system, but additional simulations will be needed for representative RO₂ + NO systems.

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