

Behavior of Nitrogen Oxides in the Product Gases from Explosive Detonations

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Abstract

All explosive materials produce a cloud of reaction products, the most toxic of which is nitrogen dioxide (NO_2). In the study reported here, 4.5-kg (10-lb) charges of blasting agent confined in either thin-wall 10-cm (4-in) diameter galvanized pipe or 10-cm (4-in) schedule 80 seamless steel pipe were detonated in a closed chamber. The detonation gases were analyzed for NO_2 , nitric oxide (NO), ammonia (NH_3), hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), and methane (CH_4). Data were evaluated to determine the kinetics of the oxidation of NO to NO_2 . Analysis revealed that the only mechanism for NO loss for the conditions existing in the chamber was the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. The rate constant was $2.08 \pm 10^{-38} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$ for the rate equation $-\frac{1}{2} \frac{d[\text{NO}]}{dt} = K \approx [\text{NO}]^2 \approx [\text{O}_2]$ for NO concentrations up to 100 ppm. The rate constant is in agreement with that recommended by Baulch, Drysdale, and Horne (1973).

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Background

In recent years, the toxic fumes generated by explosives have been a concern of blasters, explosive manufacturers, and mining companies. In the western U.S., blasters have been looking for ways to control the generation of NO₂, a very toxic gas that can be produced by large blasts at surface coal mines. Cast blasts, some employing as much as nine hundred thousand kg (two million lb) of explosive, may generate reddish-orange product clouds. The color is due to the NO₂ in the cloud (Turcotte, Yang, Lee, Short, and Shomaker, 2002).

The Occupational Safety and Health Administration's Permissible Exposure Limit (OSHA PEL) for NO₂ is 5 parts per million (ppm) and the concentration Immediately Dangerous to Life or Health (IDLH) is 20 ppm (NIOSH, 1997). The corresponding numbers for NO are 25 and 100 ppm, respectively. The study reported here deals mostly with NO₂ since it is five times more toxic than NO. The National Institute for Occupational Safety and Health (NIOSH) Documentation for IDLH Concentrations (NIOSH, 1995) states that 10 to 20 ppm NO₂ may be mildly irritating (Patty, 1963), exposure to 150 ppm or more may cause death from pulmonary edema (NRC, 1979), and 50% lethality may occur following exposure to 174 ppm for 1 hour (Book, 1982). For the past five years, the NIOSH Pittsburgh Research Lab (PRL) has been studying the toxic fumes produced by explosives and researching techniques for minimizing the fumes generation (Mainiero, 1997), (Rowland and Mainiero, 2000), (Rowland, Mainiero, and Hurd, 2001), and (Sapko, Rowland, Mainiero, and Zlochower, 2002).

During a meeting with safety personnel from several western mines in which techniques to minimize NO₂ production from blasting were discussed, several people asked how rapidly the NO produced in the blast oxidizes to NO₂. The authors were unable to find any literature specific to the kinetics of NO oxidation in gaseous detonation products. There was, however, a wealth of data available on the oxidation of NO to NO₂ in power plant plumes and gaseous emissions from other combustion processes. In this literature, the concern was not with the toxicity of NO₂ since the concentrations were very low, but rather the contribution of NO₂ to acid rain, smog formation, global warming, and ozone layer depletion (Tomita, 2001) and (Date, Yoshiaki, Arai, and Tamura, 1998).

Elshout and Beilke (1984) suggest that for the conditions existing in the detonation products in PRL's research, i.e. NO concentrations of 50-150 ppm and the absence of ozone, NO will oxidize by the following reaction:



Based on this reaction, two molecules of NO₂ are produced when two molecules of NO react with one molecule of oxygen. The reaction is said to be second order with respect to the NO concentration and first order with respect to the O₂ concentration because two molecules of NO have to come together with one molecule of O₂. The rate of NO loss and NO₂ production may be expressed as:

$$\text{Rate of NO}_2 \text{ production} = \frac{1}{2} \text{Rate of NO loss} = K [\text{NO}]^2 [\text{O}_2] \quad (2)$$

where [NO] and [O₂] represent the concentrations of nitric oxide and oxygen, respectively, and K is the rate constant for the reaction. Using equation (2) it is possible to predict the rate at which NO oxidizes to NO₂ based on the NO and O₂ concentrations. This is of limited value in the field since the

concentration of NO is usually not known but it is essential if one is to develop a computer model of the reactions occurring in a cloud of gaseous detonation products.

To verify the order of the oxidation reaction relative to NO concentration, equation (2) may be rewritten as follows:

$$-\frac{1}{2} \frac{d[\text{NO}]}{dt} = K \equiv [\text{NO}]^i \equiv [\text{O}_2], \quad (3)$$

where i is the order relative to NO, and

$$\log(-\frac{1}{2} \frac{d[\text{NO}]}{dt}) = \log(K \equiv [\text{NO}]^i \equiv [\text{O}_2]) = i \log([\text{NO}]) + \log(K \equiv [\text{O}_2]) \quad (4)$$

Examination of equation (4) reveals that a plot of $\log(-\frac{1}{2} \frac{d[\text{NO}]}{dt})$ versus $\log[\text{NO}]$ should yield a straight line with slope i and intercept $\log(K \equiv [\text{O}_2])$. Once the value of i is verified, a plot of $-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ against $[\text{NO}]^i \equiv [\text{O}_2]$ should yield a straight line of slope K .

Baulch et al. (1973) reviewed the available literature data for equation (2) and recommended a rate constant of $3.3 \times 10^{-39} \exp(530/T) \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$, for the temperature range 273 - 660 deg K. The data collected in the experiments at PRL were evaluated to determine whether they agreed with the proposed reaction and the recommended rate constant.

Method

A facility for detonating large confined charges in a controlled volume exists in the PRL's Experimental Mine for measuring fumes produced by explosive detonations (Mainiero, 1997), (Rowland and Mainiero, 2000), (Rowland et al. 2001), and (Sapko et al. 2002). Tests are conducted with a thin-wall 4-in (10-cm) diameter galvanized pipe to simulate light charge confinement and a nominal 4-in schedule 80 seamless steel pipe to simulate heavier charge confinement. The facility, illustrated in Figure 1, consists of a portion of mine entry enclosed between two explosion-proof bulkheads. Total volume of the chamber is 274 m³ (9,667 ft³). The chamber is equipped with an air circulating system and is vented by opening the vent ports to the mine's airflow. Up to 4.5-kg (10-lb) charges can be detonated in the chamber.

For a typical experiment, a blasting agent is confined in the 4-in (10-cm) schedule 80 seamless steel pipe or a thin-wall 4-in (10-cm) diameter galvanized pipe and is initiated by a Pentolite booster 2-in (5.1-cm) in diameter and 2-in (5.1-cm) thick. This combination of confinement and initiation yields a detonation velocity of approximately 4,000 m/s (13,000 ft/sec) for a 71-cm (28-in) column of a mixture of 94 pct ammonium nitrate prills with 6 pct fuel oil (94/6 ANFO) for shots in the schedule 80 pipe and approximately 2,800 m/s (9,100 ft/sec) for shots in the galvanized pipe. The pipe is suspended vertically above a heavy steel plate on the mine floor with twenty-four 1.2-m (4-ft) by 0.3-m (1-ft), 5.1-cm (2-in) thick steel plates suspended around it to form a cage. This cage stops shrapnel from the schedule 80 steel pipe that would otherwise seriously damage the chamber.

After the detonation a circulating fan is run for about 10 minutes to uniformly mix the chamber

atmosphere. Fume samples are taken out of the chamber for analysis through 6-mm (0.25-in) Teflon tubing via sampling pumps. Vacutainer gas samples are then taken and sent to the analytical laboratory for gas chromatographic analysis. This type of analysis is appropriate for components that are stable in the Vacutainer, namely H_2 , CO , CO_2 , N_2 , O_2 , and CH_4 . NO and NO_2 are measured with an on-line chemiluminescence analyzer, and NH_3 is measured with an MSA Chillgard[®] analyzer. The fumes are sampled for a 73-min. period.

The data reported in this paper were collected during 2002 as part of a study of factors affecting the toxic fumes released by the detonation of blasting agents. During evaluation of the data the authors realized that the data could also be used to develop a better understanding of the kinetics of NO_x in the product cloud from a detonation. The analysis reported here was based on 17 experiments. For each experiment, 17 datapoints were utilized. In calculating the rate of NO loss, the first two and last four data points were not utilized in order to avoid start up and shut down errors. Table 1 illustrates the data for a typical experiment.

Discussion

Figure 2 shows a plot of the NO concentrations as a function of time for the data in Table 1. As one would expect, the NO decreases with time as it is oxidized to NO_2 . If one NO_2 molecule is produced for every molecule of NO oxidized, one would expect the curve for NO_2 to be a mirror image of that for NO . However, Figure 2 shows that the curve for NO_2 is not a mirror image of that for NO . This result suggests the existence of a process by which NO_2 , and possibly NO , are removed. The plots of NO and NO_2 concentrations as a function of time showed similar behavior for the other experiments.

The data for 16 of the 17 experiments performed in the mine chamber during 2002 are plotted as $\log(-\frac{1}{2}d[\text{NO}]/dt)$ against $\log[\text{NO}]$ in Figure (3). The data for one experiment in the mine chamber were lost due to an instrumentation failure. Also, the data for the first and last 10 minutes of sampling were not used in order to avoid start-up and shut-down errors.

Conducting a regression analysis on the data in Figure (3) yields a slope of 2.04, a y-intercept of -17.35, and an r-squared value of 0.97. This confirms that the reaction is second order relative to NO . It was not possible to verify that the reaction is first order relative to O_2 since there was very little variation in O_2 from shot to shot as all shots were carried out in air. The data utilized in Figure (3) were in units of molecules, cm, and sec.

Determination of the rate constant may be accomplished by plotting $-1/2d[\text{NO}]/dt$ versus $[\text{NO}]^2[\text{O}_2]$, as illustrated in Figure (4). Conducting a regression analysis on the data yields a slope of $2.08 \times 10^{-38} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$, a y-intercept of $3.59 \times 10^{10} \text{ molecules cm}^{-3} \text{ sec}^{-1}$, and an r-squared value of 0.95. The slope is the rate constant, K , of equation (2).

Evaluation of the 272 data points for the 16 experiments in the mine chamber yielded results that are consistent with reaction (1). At the 15 deg C temperature of the mine, Baulch et al. (1973) recommend a rate constant of $2.08 \times 10^{-38} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$. The rate constant determined for the experiments in the mine chamber, $2.08 \times 10^{-38} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$, agreed perfectly with that recommended by

*Reference to specific products is for informational purposes and does not imply endorsement by NIOSH.

Baulch et al. (1973).

Before any analyses of the reaction mechanism and rate constants for NO oxidation to NO₂ could be carried out, it was necessary to determine whether NO was being removed by any mechanism other than NO oxidation. Dubnov et al. (1988) discuss this topic in the book, Industrial Explosives (Dubnov, Bakharevich, and Romanov, 1988):

With the detonation of an explosive under laboratory conditions in a vacuum vessel, colorless NO is formed, which on contact with air converts to colored oxides: nitrous anhydride (N₂O), NO₂, nitrogen tetroxide (N₂O₄). In mine conditions they are formed simultaneously and in approximately equal quantities of NO₂ and NO. The latter can remain in the loosened rock for long periods, and only changes gradually to the dioxide. NO₂ is easily dissolved in water, and therefore its concentration in the atmosphere falls as it is rapidly absorbed by moist surfaces. NO dissolves little in water.

The observations of Dubnov et al. (1988) were confirmed in research conducted by Harris, Sapko, and Mainiero (2003) which concluded that the NO concentration in explosive fumes confined in a chamber remains essentially constant if no air is present to oxidize the NO to NO₂. Based on this information, it is safe to assume that NO concentration in explosive fumes decreases mainly by oxidation to NO₂, while NO₂ concentration decreases as it is absorbed onto moist surfaces. The authors searched the literature for a method to estimate how fast NO₂ would be absorbed onto damp surfaces in the mine. There was extensive information on the absorption of NO₂ into water droplets in the atmosphere as a precursor to the production of acid rain but no information could be found for the absorption onto damp surfaces.

Blasters are aware that the gases produced by a blast are unhealthy and typically wait for the gases to dissipate before allowing anyone to return to the blast area. Less consideration is given to the NO that remains in the muck pile. The gases in the muck pile are predominately blasting fumes and do not dissipate. On the surface, the NO from the blast oxidizes to NO₂ which is readily absorbed onto wet surfaces, thereby removing it from the site. In the low-oxygen environment in the muck pile, the NO does not oxidize to NO₂. Lazarov, Brinkley, and Tole (1975) measured CO and NO_x concentrations 1.5 to 10 m (5 to 33 ft) below the surface of a muck pile for times up to 100 hours following a blast. NO_x ranged from 30 to 250 ppm and fell to safe levels in 2 to 6 hours. Miners must be aware that the NO_x will be released during the mucking operation with the potential for serious injury or death.

Summary

The NO oxidation reaction proposed by Elshout and Beilke (1984) shows promise as a means to predict the conditions existing in a cloud of detonation products. Following the detonation of an explosive in a mine chamber, the NO is removed by slow oxidation to NO₂ by the reaction



The rate at which NO oxidizes in a cloud of detonation products may be defined by equation 2 with a rate constant at 15 deg C of $2.08 \times 10^{-38} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$, which agrees with that recommended by Baulch, et al. (1973).

$$-\frac{1}{2}d[NO]/dt = K \cong [NO]^2 \cong [O_2] \quad (2)$$

The rate constant at other temperatures may be determined by the Baulch et al. (1973) recommended rate constant of $K = 3.3 \times 10^{-39} \exp(530/T) \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1}$. The data from the mine fumes chamber investigated NO concentrations up to 100 ppm. The conclusions reached in this study may or may not apply at NO concentrations above 100 ppm. The information on NO oxidation kinetics provided in this paper will prove useful in efforts to model the behavior of NO and NO₂ in clouds of detonation products near blasting operations.

Sample Time	NO	NO2	NOx	log(-dNO/dt)	log(NO)
Minutes After Detonation	PPM	PPM	PPM		
5	185.0	70.0	255.0	PPM	PPM
10	126.0	76.0	202.0	70.0	255.0
13	107.4	77.2	184.6	76.0	202.0
16	93.7	77.6	171.3	12.21	15.40
19	83.0	77.0	160.0	12.17	15.35
22	74.6	75.7	150.3	12.07	15.30
25	67.8	73.9	141.7	11.98	15.26
28	62.1	72.4	134.5	11.90	15.22
31	57.1	69.4	126.5	11.83	15.19
34	53.1	67.8	120.9	11.77	15.15
37	49.4	65.8	115.2	11.71	15.12
40	46.1	62.3	108.4	11.67	15.09
43	43.3	60.1	103.4	11.61	15.07
46	40.6	57.5	98.1	11.56	15.04
49	38.4	55.3	93.7	11.51	15.01
52	36.4	53.3	89.7	11.46	14.99
55	34.5	51.3	85.8	11.42	14.97
58	32.9	50.0	82.9	11.40	14.95
61	31.3	48.5	79.8	11.38	14.92
64	29.9	47.0	76.9		
67	28.6	45.5	74.1		
70	27.4	44.3	71.7		
73	26.3	42.8	69.1		

Table 1. Data collected in a typical experiment in the mine fumes chamber.

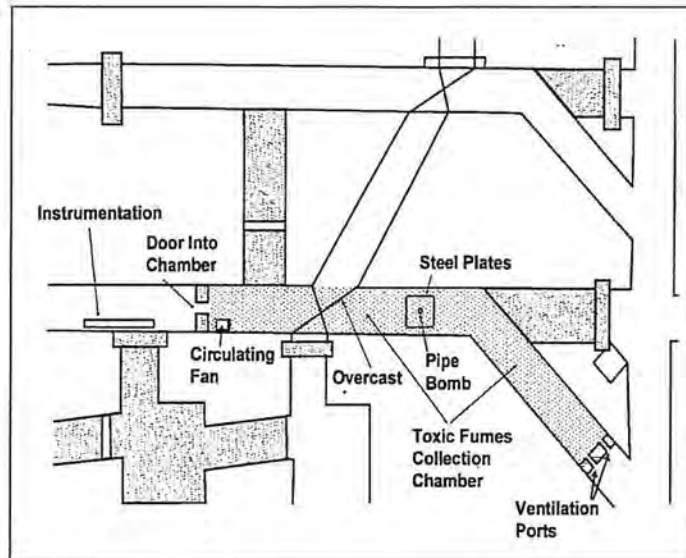


Figure 1. Chamber in the underground mine at the NIOSH Pittsburgh Research Lab in which the gaseous products of a 10-lb explosive detonation are confined.

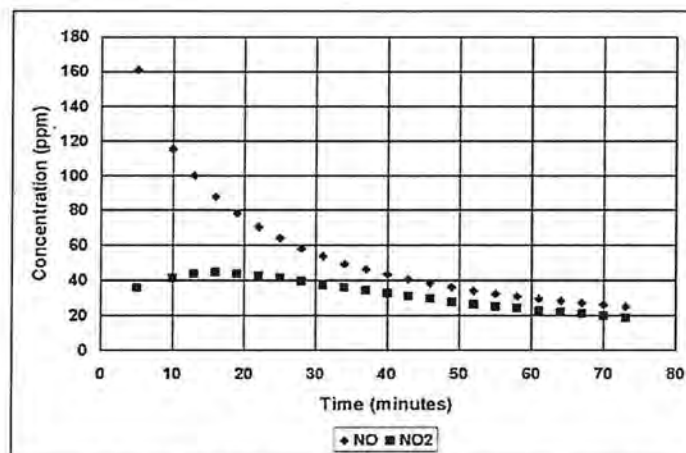


Figure 2. Plot of NO and NO₂ versus time for the data of Table 1.

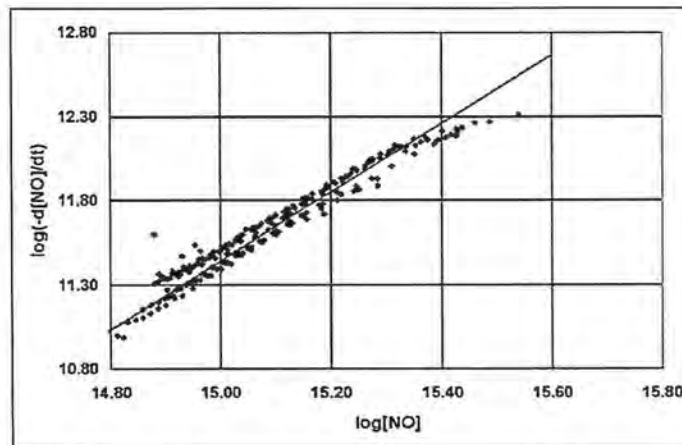


Figure 3. Plot of $\log(-\frac{1}{2} \frac{d[\text{NO}]}{dt})$ versus $\log[\text{NO}]$ for experiments in the mine chamber during 2002. The line represents the regression fit to the data.

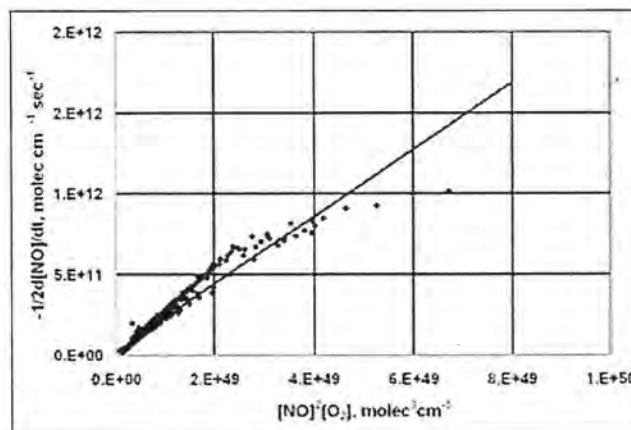


Figure 4. Plot of $-1/2 \frac{d[\text{NO}]}{dt}$ versus $[\text{NO}]^2 [\text{O}_2]$ for experiments in the mine chamber during 2002. The line represents the regression fit to the data.

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