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# Kinetics of PBX9404 Aging

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## Disclaimer

# Kinetics of PBX9404 Aging[*]

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PBX 9404 is an early formulation of HMX from which we can learn about the effects of aging in the weapons stockpile. Of particular interest is the presence of 3% nitrocellulose in PBX 9404 as an energetic binder. Nitrocellulose is used pervasively in smokeless gunpowders and was formerly used extensively in the film and art preservation industries. It is well known that nitrocellulose decomposes autocatalytically, and stabilizers, such as the diphenylamine used in PBX 9404, are used to retard its decomposition. Even so, its lifetime is still limited, and the reactions eventually leading to catastrophic autocatalysis are still not understood well despite years of work.[1] In addition to reducing the available energy in the explosive, degradation of nitrocellulose affects the mechanical properties of the pressed PBX 9404 parts by the associated reduction in molecular weight, which reduces the strength of the binder.

A structural formula for a monomer of the nitrocellulose used in PBX 9404 is shown in Figure 1. The initial nitration level is 2.3 of 3.0 possible sites, and they have different reactivities.[2] Degradation of nitrocellulose affects many properties. As an aid in examining historical chemical analysis data, several measures of degradation are given in Table 1 for the simple replacement of a nitro group with a hydrogen. The weight percent of nitrocellulose remaining for an initial concentration of 3% as used in PBX 9404 is also given. Of course, the real degradation reaction is more complicated, including chain scission and crosslinking reactions giving other gas species.

During the course of this work, we spent considerable time addressing the question, “Why is PBX 9404 blue?” There was actually considerable controversy in the color evolution with aging, and the situation was clarified by Ben Richardson at Pantex. Workers there assured us that PBX 9404 starts with an ivory color. Drying the prill prior to pressing turns it a mottled blue, and well-preserved prill samples retain a blue color decades after formulation. Subsequently, heat and light both send it through a progression of colors from grayish blue, blue-green, green, brown, dirty yellow, mottled tan, and eventually pale tan. The progression is accelerated by oxygen and possibly moisture, as has been shown in several accelerated aging studies. The precise compounds causing the color evolution are uncertain, but they are undoubtedly a progression of quinoidal, nitroso, and nitrated DPA compounds. For example, paranitroso DPA is deep blue. Unfortunately, the location of various nitrated DPAs, which ranged from yellow to orange to red to brown and which were used by Pantex as analytical standards in the 1970s, is not currently known.

While the color change is indicative of aging, it is by no means a quantitative measure of the extent of nitrocellulose degradation. Inspection of the literature yielded a

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variety of kinetic models, and the activation energy typically ranges from 25-35 kcal/mol for T<100 $^{o}$C. This literature qualitatively predicts times for 30% decomposition ranging from a few days at 100 $^{o}$C to 1-2 years at 50 $^{o}$C to 50 years at room temperature. To develop a quantitative model, we used the data of Leider and Seaton,[3] which were collected at conditions most closely matching stockpile conditions for any data set we had available. They used PBX 9404 heated as pressed pellets in closed vessels at temperatures ranging from 50 to 100 $^{o}$C for times up to three years, and they report mass loss, gas yield and composition, and chemical analysis of the residual solid by methods used in stockpile surveillance.

Initial kinetic analysis of the weight of remaining nitrocellulose as measured by liquid chromatography and the loss of nitrate esters by a colorimetric technique gave an activation energy of 27 kcal/mol. However, the reaction is complex due to the different stability of the three nitroester positions, and this complexity required either parallel first-order reactions or an nth-order reaction (n=3.6), which is mathematically equivalent to a Gamma distribution of frequency factors, to match the deceleratory character of conversion versus time curves. This model fit the data up to about 60% conversion, when rapid autocatalysis sets in (Figure 1).

Next, a sequential first-order model was developed to match the remaining mass of nitrocellulose, its empirical formula, and the yield of various gases. Details of that chemical reaction model are shown in Figure 3. One caveat is in their use is that the solubility of nitrocellulose decreases substantially for nitrogen contents less than 6 wt%. One might suspect solubility as the cause for the rapid increase in nitrocellulose decomposition rate in nitrocellulose at 60% conversion, but that decrease is accompanied by a sharp increase in gas production, so it truly represents a chemical autocatalytic process.

1. T. B. Brill and P. E. Gongwer, Prop. Expl. Pyrotech. 22, 38-44 (1997).
2. H. R Leider and A. J. Pane, Differential Decomposition of the Three Ester Sites in Cellulose Nitrate and the Accelerated Decomposition of Highly Esterified Cellulose Nitrates, LLNL preprint UCRL-96795 (June 1987).
3. H. R. Leider and D. L. Seaton, “Gas Evolution and Weight Loss From Thermal Decomposition of PBX-9404 Below 100 $^{o}$C,” LLNL Report UCRL-52692 (March 1979).

**Table 1.** Cross comparison of various measures of nitrocellulose composition referenced to the lacquer grade used in PBX 9404.

| Fraction of NC mass remaining | N/C atomic ratio | % Denitration | Wt% N | Wt% NC |
|---|---|---|---|---|
| 100 | 2.3 | 0 | 12.13 | 3.00 |
| 95 | 2.0 | 13 | 11.11 | 2.85 |
| 86 | 1.5 | 35 | 9.15 | 2.59 |
| 80 | 1.1 | 52 | 7.28 | 2.39 |
| 75 | 0.8 | 65 | 6.22 | 2.24 |

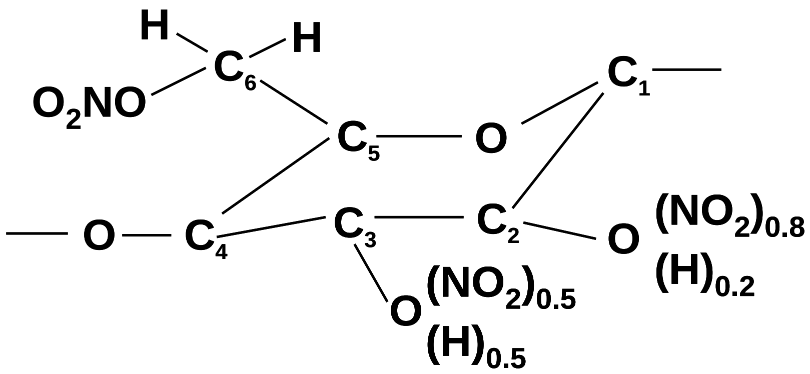


**Fig. 1.** Structural formula of a nitrocellulose monomer. The $C_6$ position nitrates first and decomposes the slowest. The C2 position decomposes the fastest.[2]

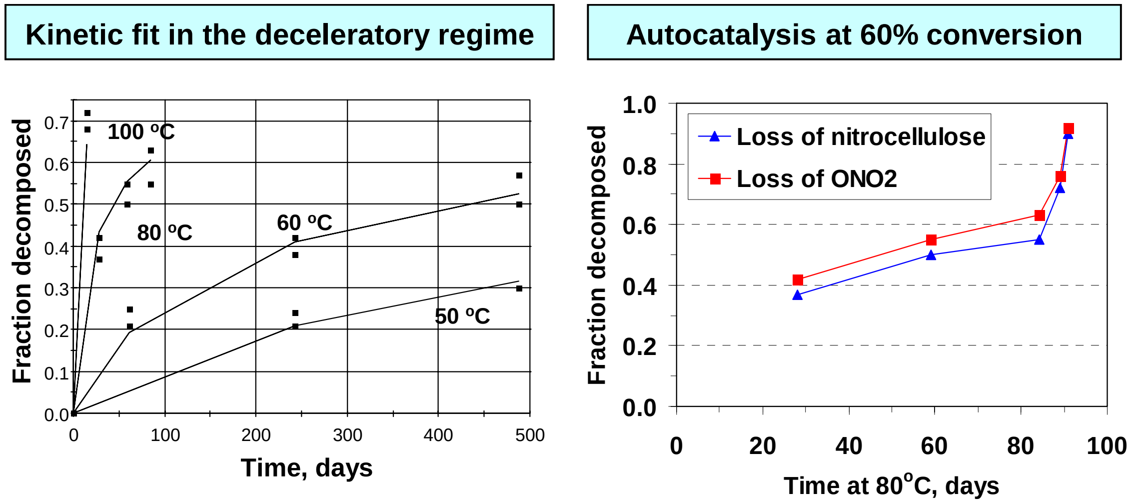
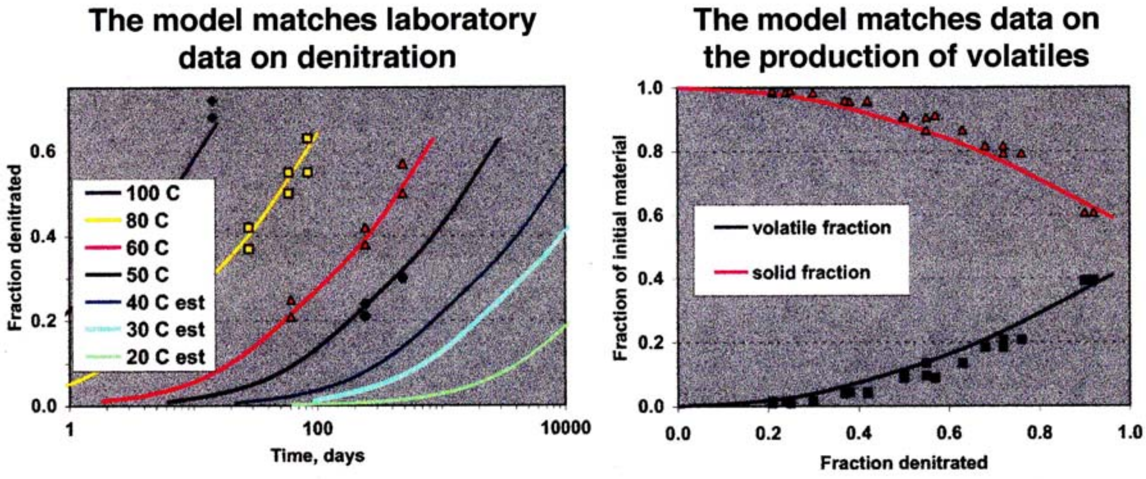


**Fig. 2.** Global kinetic analysis of nitrocellulose, giving $k = 2.7\times10^{10} \exp(-13575/T)\ s^{-1}$ and an apparent reaction order of 3.6. The points are the experimental data, and the solid line connect the calculated points.



|  |  |
|---|---|
| 0-20%: | relatively rapid kinetics for denitration; minor mass loss |
| 20-60%: | denitration is decelerating; DPA is saturated, leading to more mass loss |
| 60-100%: | drastic acceleration in decomposition rate (not modeled). |

| Rate expression, $s^{-1}$ | Empirical formula | Mass partitioning |
|---|---|---|
| $3.5\times10^{10}\, e^{-13085/T}$ | $C_6H_{7.7}N_{2.3}O_{9.6} \rightarrow C_{5.95}H_{7.99}N_{1.9}O_{8.76}$ + nitrated DPA + 0.001 $N_2$ + 0.024 $N_2O$ + 0.012 CO + 0.035 $CO_2$ + 0.03 $H_2O$ | 0.9275 NC, 0.0593 nitrated DPA, 0.0132 gas |
| $3.5\times10^{9}\, e^{-13085/T}$ | $C_{5.96}H_{7.99}N_{1.9}O_{8.76} \rightarrow C_{5.60}H_{7.29}N_{1.16}O_{7.64}$ + 0.25 $N_2$ + 0.12 $N_2O$ + 0.05 CO + 0.3 $CO_2$ + 0.35 $H_2O$ | 0.1347 gas, 0.8653 solid |
| $6.0\times10^{8}\, e^{-13085/T}$ | $C_{5.60}H_{7.29}N_{1.16}O_{7.64} \rightarrow C_{4.68}H_{5.69}N_{0.16}O_{4.77}$ + 0.15 $N_2$ + 0.35 $N_2O$ + 0.12 CO + 0.8 $CO_2$ + 0.8 $H_2O$ | 0.3405 gas, 0.6595 solid |

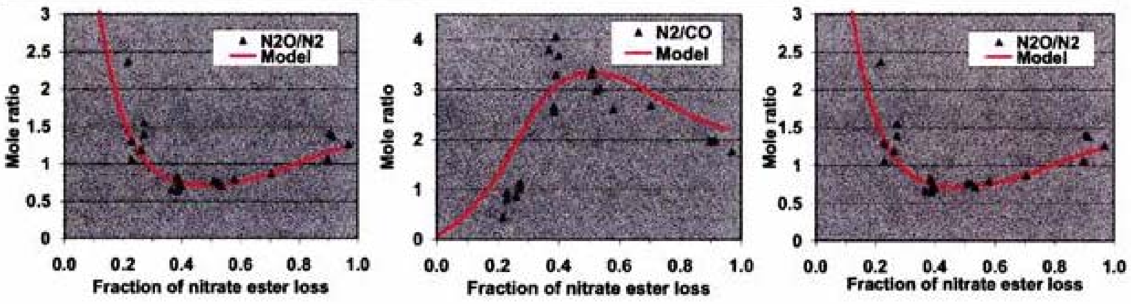


**Fig 3.** Description of the sequential degradation model, including a comparison to gas yield and composition. Extrapolation to 30 °C indicates ~40% denitration over 27 years.