Klapötke, Answers to the study questions from the graduate-level textbook
Chemistry of High-Energy Materials, 4th edition, De Gruyter, Berlin/Boston, 2017
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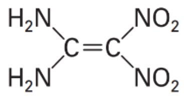
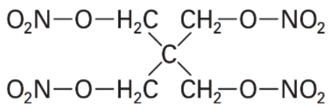
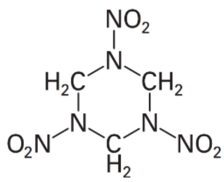
Answers

1. FOX-7: 

   PETN: 

   RDX: 

2. 4.3 m

3. single base gun propellant: NC (12.5%)
   double base gun propellant: NC : NG (50 : 50)
   triple base gun propellant: NC : NG : NQ (25: 25: 50)

4. One fundamental problem for formulations containing red phosphorus and magnesium, in particular in formulations which contain a substoichiometric quantity of oxidizer, is that a thermodynamically favourable side-reaction between the phosphorus and the magnesium can occur:

   $$2\ P + 3\ Mg \rightarrow Mg_3P_2$$

   The magnesiumphosphide that is subsequently formed can react with atmospheric moisture to form phosphine which is toxic:

   $$Mg_3P_2 + 6\ H_2O \rightarrow 3\ Mg(OH)_2 + 2\ PH_3$$

   This unwanted reaction can also occur very slowly if smoke munition is stored for several years, which can result in a considerable contamination of the munition depot (mainly bunkers or tunnel-shaped caves) with gaseous PH_3.

5. enthalpies of formation: Gaussian09
   detonation parameters: EXPLO5
   Cheetah 5.0

6. For a compound with the general formula $C_aH_bN_cO_d$, the oxygen balance Ω (in %) is defined as follows:

$$\Omega_{CO_2} = \frac{[d - (2a) - \left({}^{b}/_{2}\right) \times 1600}{M}$$

$d = 6$
$a = 2$
$b = 4$
$M = 152$
$\Omega = 0$

7. $$\sqrt{2E} = \frac{3\sqrt{3}}{16}\, D \approx \frac{D}{3.08}$$
$$\sqrt{2E} = 2.922 \text{ m s}^{-1}$$

8. DU
reason: Higher density of DU. The Bernoulli equation shows the relationship between the penetration depth (P) and the length of the penetrator (L) with the densities of the penetrator (ρ_P) and the target (ρ_T):

$$P \sim L\sqrt{\frac{\rho_P}{\rho_T}}$$

9. The N_2/CO ratio should be high.
T_c should be low.

10. The impact energy is: E = energy = work × distance = mass × acceleration × distance, therefore:
E = 5 kg × 9.81 m s^{-2} × 0.5 m = 24.5 kg m^2 s^{-2} = 24.5 Nm = 24.5 J

11. – mixed acid
– nitric acid, HNO_3 (65 – 100%)
– dinitrogen pentoxide, N_2O_5
– $NO_2^+BF_4^-$, nitronium tetrafluoroborate
– $NO_2^+OSO_2CF_3^-$, nitronium triflate
also: Ag salts, $AgNO_3$, $AgNO_2$ or KNO_3 / oleum (H_2SO_4/SO_3)

12. – for bipropellants in rocket propulsion, especially but not exclusively for pulsed mode operation
– for incendiary devices

13. DNAN = dinitroanisole
or
IMX-101: DNAN = dinitroanisole (binder) + NTO (filler)

14. IMX-104: DNAN (binder) + NTO and RDX (filler)

15. $$I_{sp} \sim \sqrt{\frac{T_c}{M}}$$

16. $$\bar{F} = I_{sp}\frac{\Delta m}{\Delta t}$$

Where I_{sp} is the specific impulse in (m s^{-1}), Δm is the mass of used propellant (in kg) and Δt is the duration of burning of the engine (in s).

17. double-base: NC/NG formulation (homogeneous)
composite: AP, Al, HTPB binder (heterogeneous)

18. 20 s

19. This is the NIR range. Suitable metals are Cs (caesium) and K (potassium).

20. Kamlet-Jacobs equation:

$$p_{\text{C-J}}\ [\text{kbar}] = \mathrm{K}\,\rho_0^2\phi$$

$$p_{\text{C-J}} \sim \rho_0^2$$

21. Both values can be estimated using Trouton's rule, where T_m is the melting point of the solid and T_b is the boiling point of the liquid:

$$\Delta H_{\text{sub.}}\ \left[\text{J mol}^{-1}\right] = 188\ T_{\text{m}}\ [\text{K}]$$
$$\Delta H_{\text{vap.}}\ \left[\text{J mol}^{-1}\right] = \ 90\ T_{\text{b}}\ [\text{K}]$$

22. The Bernoulli equation shows the relationship between the penetration depth (P) and the length of the penetrator (L) with the densities of the penetrator (ρ_P) and the target (ρ_T):

$$P \sim L\sqrt{\frac{\rho_P}{\rho_T}}$$

23. The Gurney velocity $\sqrt{2\mathrm{E}}$ and the detonation velocity (D = VoD) of an explosive can be described approximately using the following simple relationship:

$$\sqrt{2\mathrm{E}} = \frac{3\sqrt{3}}{16}D \approx \frac{D}{3.08}$$

24. Technical N_2O_5 was previously mainly obtained by the dehydration of nitric acid at –10 °C, as N_2O_5 is the anhydride of nitric acid. It is an easily sublimed solid (subl. 32 °C, 1 bar).

$$4\ HNO_3 + P_4O_{10} \rightarrow 2\ N_2O_5 + 4\ H_3PO_4$$

Since 1983, the technical synthesis usually used has followed that developed by Lawrence Livermore National Laboratory, in which the electrolysis of nitric acid in the presence of N_2O_4 results in the formation of a ca. 15–20 % solution of N_2O_5 in anhydrous nitric acid.

$$2\ HNO_3 \xrightarrow{N_2O_4,\ -2e^-} N_2O_5 + H_2O$$

Pure and almost acid-free N_2O_5 can be obtained from the gas-phase ozonation of N_2O_4 using an ozone-oxygen mixture with a ca. 5–10 % ozone content.

$$N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$$

25. ADN is synthesized by the nitration of ammonia using N_2O_5 (prepared by the ozonation of NO_2) in a chlorinated solvent:

Synthesis of N_2O_5:

$$2\ NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

Synthesis of ADN:

$$NH_3 + N_2O_5 \rightarrow (O_2N)NH_2 + HNO_3$$
$$(O_2N)NH_2 + N_2O_5 \rightarrow (O_2N)_2NH + HNO_3$$
$$(O_2N)_2NH + NH_3 \rightarrow [NH_4^+][N(NO_2)_2]^-$$
$$2\ HNO_3 + 2\ NH_3 \rightarrow 2\ [NH_4^+][NO_3]^-$$

$$4\ NH_3 + 2\ N_2O_5 \rightarrow [NH_4^+][N(NO_2)_2]^- + 2\ [NH_4^+][NO_3]^-$$

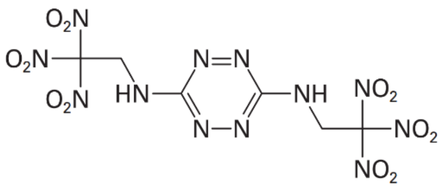
26. The biocidal activity of HF exceeds that of both Cl_2 and HCl. 200 ppm HF destroy most bacteria, including Anthrax spores.

27. $M_xO_y + Al \rightarrow M + Al_2O_3$

28. Lead-free tetrazolate based primary explosive are:

    – Cu(I) nitrotetrazolate, DBX-1
    – Cu(II) 1-methyl-5-nitriminotetrazolate
    – $[Na]_2$ $[(H_2O)_2Cu(nitrotetrazolate)_4]$

29. Bis(trinitroethyl)-1,2,4,5-tetrazine-3,6-diamine (BTAT)



30. Decrease of thyroxin synthesis due to inhibition of iodine storage.

31. Underwater operations, torpedo propulsion.

32. Solid rocket motor: 3000–4000 bar
    Large calibre gun: 40–70 bar

33. a)
    – heat of explosion Q (in kJ kg^{-1}),
    – detonation velocity D (in m s^{-1}),
    – detonation pressure P (in kbar),

    and less importantly,

    – explosion temperature T (in K) and
    – volume of gas released V per kg explosive (in L kg^{-1}).

    b)
    – the specific energy f_E or force or impetus ($f_E = n\,R\,T$),
    – the combustion temperature T_c (in K),
    – the co-volume b_E (in cm^3 g^{-1}),
    – the pressure p (in bar; 3000–4000 bar).

    c)
    The most important performance parameter is the specific impulse I_{sp}, or I^*_{sp} with:

$$I^*_{sp} = \frac{I_{sp}}{g}$$

    The average thrust of a rocket $\bar{F}$ can in accordance with the equation above be given simply as:

$$\bar{F} = I_{sp}\frac{\Delta m}{\Delta t}$$

34. – the combustion temperature T_c, which should be low.
    – the N_2/CO ratio of the combustion gases, which should be high.

35. Target penetration of an EFP is much less than that of a jet (SC), but the hole diameter is larger with more armour backspall.

36. The gap test.

37. The fast cook-off test.

38.

	advantage	disadvantage
RDX	Higher performance	Lower thermal stability than HNS, higher sensitivity than HNS
HNS	Higher thermal stability, lower sensitivity	Lower performance

39. – very high sensitivity
    – very high vapour pressure (volatile)

40. a) isochoric
    b) isobaric
    c) isochoric

41. a) SrCl
       SrOH
    b) BaCl
       BaOH
       Ba

42. In accordance with the rule of Wien, the maximum wavelength of the blackbody radiation λ_{max} (µm) shifts towards shorter wavelengths (higher energy) with increasing temperature:

$$\lambda_{max} = 2897.756\ \mu m\ K\ T^{-1}$$

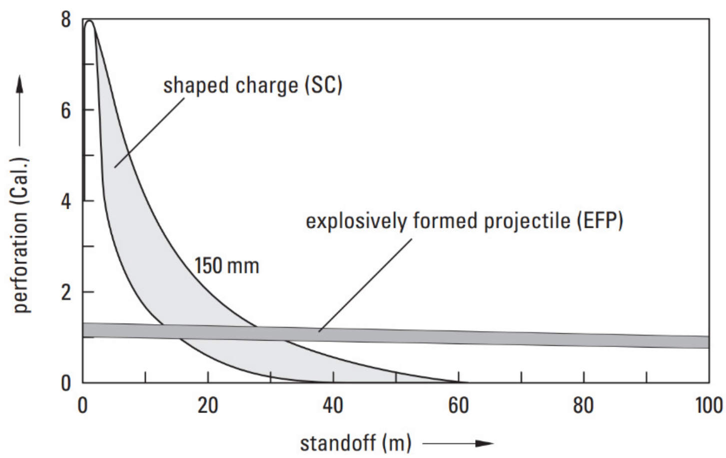
43. The burn rate increases with increasing pressure:

$$r = \beta\ p^{\alpha}$$

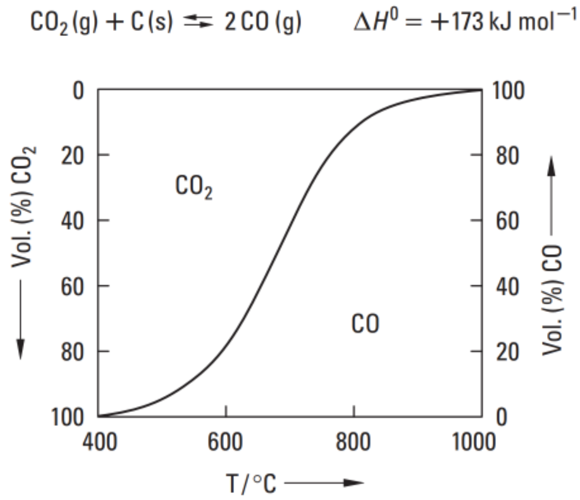
In this context, β is a coefficient ($\beta = f(T)$) and α is the index of the burn rate which describes the pressure dependency. The index α is < 1 for energetic materials which deflagrate and > 1 for detonating explosives.

44. Usually (at least in the µm region) smaller particles show a much higher sensitivity towards electrostatic discharge.

45. The main advantage of the EFP over a conventional shaped charge is its effectiveness at very large standoff distances, equal to hundreds of times the charge's diameter (perhaps a hundred meters for a practical device):



46. At high temperatures CO is thermodynamically favored over CO*2* according to the Boudouard equilibrium:



47. – oxidation of the carbon back-bone, e.g. TNT
– introduction of ring or cage strain, e.g. CL-20
– highly endothermic, nitrogen-rich compounds, e.g. TAGzT

48. nitro: TNT, HNS
nitrate (nitrate ester): NG
nitramino: RDX, HMX
nitrimino: TAG 1-MNT
azide: $Pb(N_3)_2$
peroxo: TATP

49. – in pure (liquid) form too sensitive,
– crystallizes at about 13 °C,
– in safe to handle formulations (e.g. dynamite) too low-performance.

50. Kamlet and Jacobs suggested an empirical relationship between the detonation velocity and the **detonation pressure**. In this, the detonation velocity *D* is linear and the detonation pressure $p_{C\text{-}J}$ to the power of two dependent on the loading density ρ_0 (in g cm^{-3}):

$$p_{C\text{-}J}\ [\text{kbar}] = K\,\rho_0^2\phi$$

$$D\ [\text{mm}\ \mu\text{s}^{-1}] = A\,\phi^{0.5}\,(1 + B\,\rho_0)$$

The constants K, A and B are defined as follows: K = 15.88
A = 1.01
B = 1.30

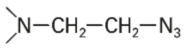
The value ϕ is therefore

$$\phi = N\,(M)^{0.5}(Q)^{0.5}$$

where – *N* is the moles of gas released per gram of explosive,
– *M* is the mass of gas in gram per mole of gas and
– *Q* is the heat of explosion in cal per gram.

51. 0.250 J = 250 mJ

52. – Oxone® (2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$; the active ingredient is: $KHSO_5$)
    – MCPBA [meta-chloro perbenzoic acid]
    – H_2O_2 / H_2SO_4
    – H_2O_2 / CF_3-COOH
    – ozone
    – HOF

53. MMH: $(CH_3)HN-NH_2$
    UDMH: $(CH_3)_2N-NH_2$
    DMAZ: 
    2-Dimethylaminoethylazide

    – hypergolic fuels (with N_2O_4 and WFNA) and bipropellants

    – MMH replacement, less toxic

54. 166.8 kN

55. EBW, EFI (also known as “slapper detonator”), hotwire detonators

56. Although electric detonators appear to be much more complicated than simple hot wire devices, the advantages of electric detonators are obvious:

    – safety, insensitivity
    – reliability
    – precision
    – repeatability
    – simultaneity
    – shot to shot reliability (under 5 microseconds).

57. MTX-1

58. DMAZ or TMTZ

59. – the shock energy from an underwater explosion measures the explosive’s shattering action in other materials (µs time-scale);
    – the bubble energy from the underwater explosion measures the heaving action of the explosive (ms time-scale).

60. $$D\ [\text{km s}^{-1}] = 1.453\ I_{sp}\ [\text{N s g}^{-1}]\ \rho_0\ [\text{g cm}^{-3}] + 1.98$$
    $$p_{C\text{-}J}\ [\text{kbar}] = 44.4\ I_{sp}\ [\text{N s g}^{-1}]\ \rho_0^2\ [\text{g}^2\ \text{cm}^{-6}] - 21$$

61. IMX-104 (DNAN + NTO + RDX)

62.

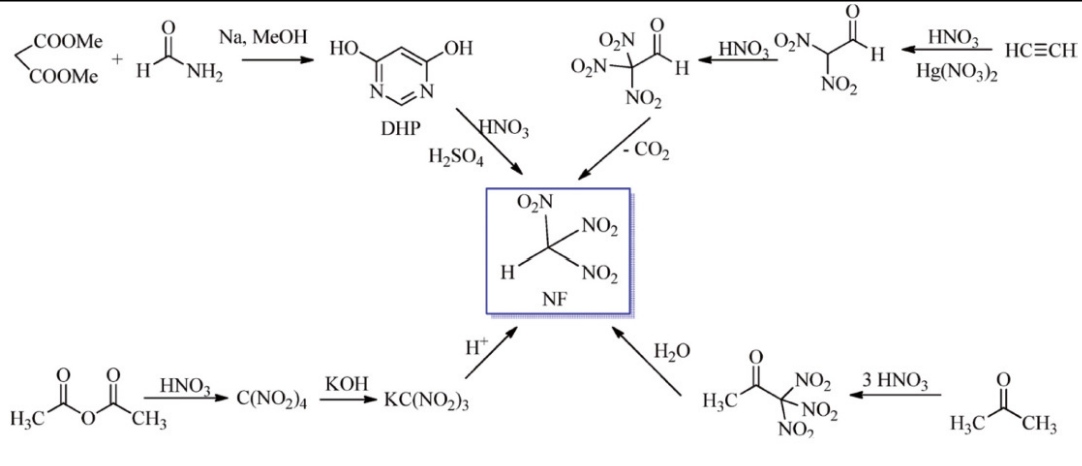


Fig. 1.20: Synthetic routes for the preparation of NF.

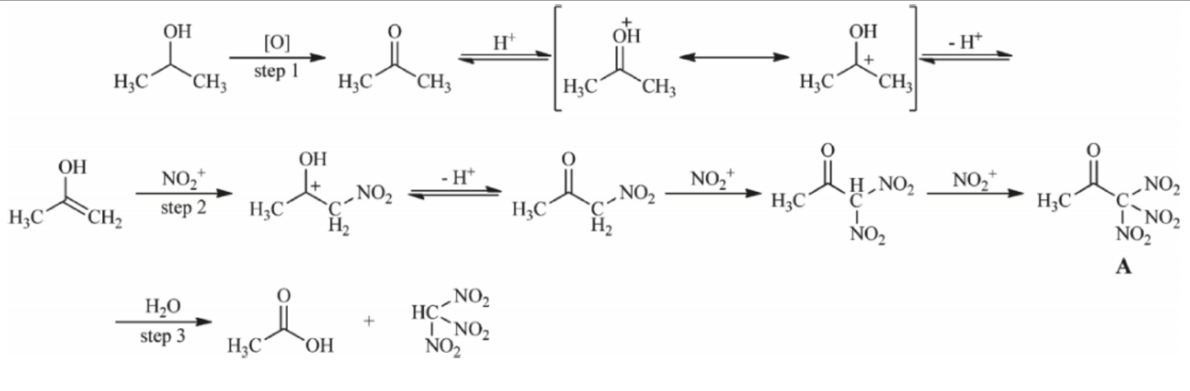


Fig. 1.21: Synthesis of NF from isopropanol in fuming nitric acid.

63.

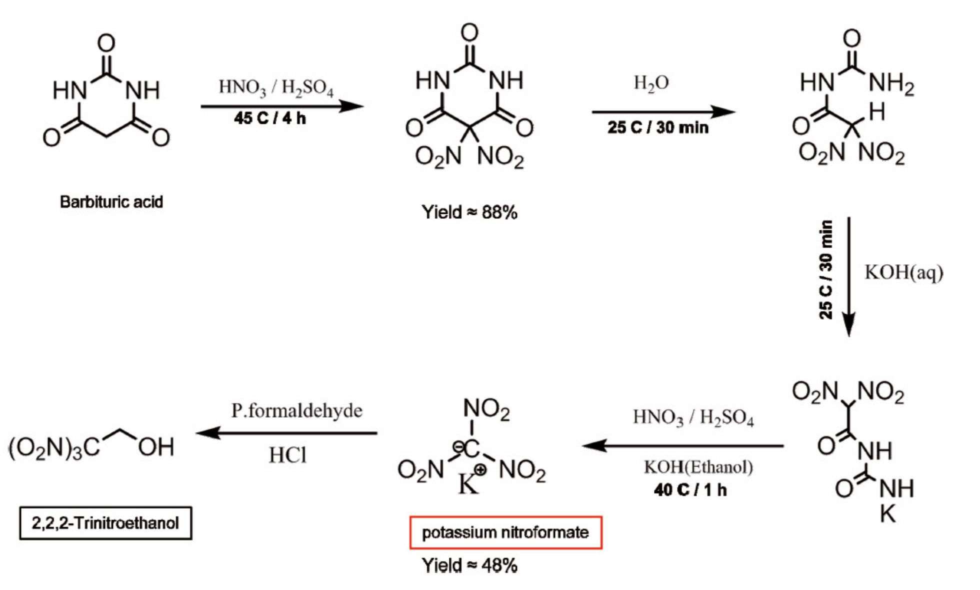


Fig. 1.22: Synthesis of TNE via potassium nitroformate.