



UV-VIS and FTIR Investigations of Long-Term Aged Explosives Part 2

Petar SHISHKOV, Milena NEDKOVA, Petia ATANASOVA
and Ivan GLAVCHEV*

*University of Chemical Technology and Metallurgy,
8 Kl. Ohtidski St., 1756 Sofia, Bulgaria*

**E-mail : ivgl@uctm.edu*

Abstract: Samples of long-term aged TD-50 and tetryl were investigated by UV-VIS and FTIR spectroscopy and bands of products of ageing were obtained. A complicated maximum of nitro groups at 1537 cm^{-1} in the FTIR spectra of long-term aged explosives was obtained, like in the IR spectra of long-term aged single-based propellants. Ageing process was confirmed by the presence of several maxima in UV-VIS and FTIR spectra of aged products and determination of several characteristics of the investigated explosives (shifts $\Delta\nu$, differences in absorbances ΔA , differences in values of $\Delta h^*_{1/2}$). Ageing was connected with decrease of H-bond formation on the base of decrease of content of oxygen and nitro groups in TD-50 and tetryl.

Keywords: long-term ageing, TD-50, tetryl, UV-VIS, FTIR, H-bond

Introduction

In the literature there is a lot of information on ageing of explosives. The stability of several explosives to Fenton and photo-Fenton processes was determined in [1] and it was established that oxidation efficiency decreased in the following sequence: DNT (2,4-dinitrotoluene) – 0.938 > PA (2,4,6-trinitrophenole) – 0.883 > AP (ammonium salt of PA) – 0.813 > TNT (2,4,6-trinitrotoluene) – 0.366 > tetryl (2,4,6-trinitrophenylmethylnitramine) – 0.294 > RDX (cyclotrimethylenetrinitramine) – 0.188 > HMX (octogen) – 0.068. R.J. Fellows et al. [2] investigated transformation of tetryl and TNT in soil and

plant systems and determined the stability of these materials. According to the authors, $-\text{NO}_2$ groups in tetryl were transformed into $-\text{NH}_2$ groups (principal transformation) or into hydrogen atoms (minor transformation). Some of these compounds were characterized by UV-VIS spectroscopy. C.D. Hutchinson et al. [3] investigated thermal decomposition of tetryl and they obtained the IR spectrum of the product made at $225\text{ }^\circ\text{C}$ – bands at 3036 and 3273 cm^{-1} . In the IR spectrum of tetryl published in [4], there was a maximum around 3450 cm^{-1} , absent in the spectrum given in [2], while in the spectrum published in [5], there was a maximum at 3700 cm^{-1} . In [4], thermal ageing of several explosives at $70\text{ }^\circ\text{C}$ was investigated and many analyses were made. As results of elemental analyses, small differences between the found values and the calculated content of carbon, hydrogen and nitrogen before the ageing of the explosives were observed. Maybe this is the reason of the presence of the maximum at 3450 cm^{-1} in the IR spectrum of tetryl. Also moisture content in the investigated sample can influence on the presence of this maximum. In the IR spectra of all the explosives investigated and published in [4], there is the same maximum and this is the reason to confirm the last supposition. In the IR spectrum published in [5], there are several mistakes and this is the reason to make only a small number of calculations. The goal of our investigations was to determine the available properties for characterization of ageing of TD-50 and tetryl connected with H-bond formation.

Experimental

Samples of TD-50 and tetryl, obtained by dismantling of weapons, were dissolved in acetone or toluene, p.a. (Merck products) to clear solutions. UV-VIS spectra were obtained with an apparatus Cary 100 Scan UV-VIS spectrophotometer (Varian, Germany). FTIR spectra were made from the thin layers of the investigated materials with a FTIR spectrophotometer (Varian, Germany) after evaporation of the solvent. The values of A_1 , A_2 , A_3 , $\Delta h^{*1}_{1/2}$, $\Delta h^{*2}_{1/2}$, $\Delta h^{*3}_{1/2}$ were calculated from the obtained spectra and from spectra published in the literature, by the methods described in our work “UV-VIS and FTIR Investigations of Long-Term Aged Explosives. Part 1”, published in this number of *CEJEM*. The values of the shifts $\Delta\nu$ and the differences in absorbances ΔA_1 , ΔA_2 and ΔA_3 were calculated as differences between the values of maxima in the obtained FTIR spectra of tetryl and from the IR spectra of tetryl published in the literature. The values of Δh^* were calculated in the same way. The spectra of the maximum for $-\text{NO}_2$ groups in FTIR spectra of TD-50 and tetryl at 1537.231 cm^{-1} were made with different scanning to determine differences after ageing.

Results and Discussion

The investigated explosives were obtained by dismantling of weapons, made in Bulgaria in 1961. The weapons were stored in non-heated military stores and the time of ageing of the explosives was around 50 years. The investigation of transformation of explosives in soil and plant systems, published in [2], determined the most available wavelength for chromatography investigation. In the UV-VIS spectrum of tetryl dissolved in acetonitrile it was shown that it was 264 nm. Next, the authors made standard curve for dependence concentration/absorption in methanol solutions of tetryl. In Figure 3.11, the authors showed ultraviolet spectrum of the transformation product 4 (wavelength 344 nm) but in this figure there was no maximum for a part of non-transformed tetryl (wavelength 264 nm). In Part 1, it was shown that the polarity of the used solvent and decrease of the concentration of solutions shifted the wavelength of tetryl. For example, toluene solutions with concentration of tetryl from 1.924 mg/ml to 0.2749 mg/ml shifted the maximum at 335 nm to 325 nm. The maximum for acetone solution with concentration of 4.873 mg/ml was at 327 nm. In the UV-VIS spectra of acetone solutions of tetryl at 263 nm and in the spectra of toluene solutions at 264 nm, there was a maximum but it was smaller than the maxima described in this work. All of these spectra have a maximum at 344 nm and this maximum shifted by decrease of the concentration of the investigated solutions. The presence of this maximum confirmed the transformation of $-\text{NO}_2$ group into $-\text{NH}_2$ group after long-term ageing of tetryl. Investigation of ageing of explosives and propellants was described in several works. In [6], it was shown that the maximum for $-\text{ONO}_2$ groups at 1660 cm^{-1} in the IR spectra of single-based propellants after long-term ageing was with complicated shape. It was interesting to make the IR spectra of the maximum for $-\text{NO}_2$ group in the investigated explosives and to compare the shape of the bands. In this way, it was possible to apply information on ageing processes of explosives. The spectra of the maxima for $-\text{NO}_2$ groups at 1537.231 cm^{-1} of the FTIR spectra of the investigated samples of TD-50 and tetryl were made with different scanning. The characteristics of these maxima are in Tables 4 and 6 in Part 1. On the other hand, it is well known that explosives change their molecular structure during ageing. It is known that TD-50 consists of 50% dinitronaphthalene [7] and that the characteristics of this material depend on the content of different isomers which depends on the applied technology of production. We have no information on the technology applied for the production of the investigated sample of TD-50. This is the reason to make calculations for ageing only from the FTIR spectra of tetryl. In this work, the FTIR spectrum of TD-50 was made to show the complicated shape of the band for $-\text{NO}_2$ group

at 1537.231 cm^{-1} . The results obtained are in Table 4 published in Part 1. The results for the FTIR spectrum of tetryl are in Table 6 in the same article. All the values were calculated with dependences described in Part 1. The maximum at 1537.231 in the FTIR spectra of TD-50 and tetryl after long-term ageing were complicated and consisted several maxima. In the FTIR spectrum of tetryl after long-term ageing there were several maxima which are not shown in Table 6. For example, the maximum at 3020.417 cm^{-1} was with absorbances $A_1= 1.2686$; $A_2= 0.811$ and $A_3= 0.7941$. In Figure 3.9 in page 38 of the work [2], the FTIR spectrum of the main product obtained after thermal transformation of tetryl was given. For $-N-H$ stretch of this product, there are maxima at 3279 and 3047 cm^{-1} and at 2837 and 2744 cm^{-1} . Because the FTIR spectrum of long-term aged tetryl given in Table 6 (Part 1) was for a mixture of transformed and non-transformed products, the maxima at 3020.417 , 2832.118 , 2682.594 and 2529.283 cm^{-1} were for transformation products of tetryl after long-term ageing. These bands were absent in the IR spectra of pure tetryl. The maximum at 3279 cm^{-1} was a part of the complicated band at 3409.984 cm^{-1} .

Calculations given in Tables 1, 2 and 3 were made for pure, non-aged tetryl from some IR spectra published in the literature.

Table 1. Values of the calculated properties of the sample of tetryl from the IR spectrum, published in [2]

No.	ν, cm^{-1}	A_1	A_2	A_3	$\Delta h^1_{1/2}$	$\Delta h^2_{1/2}$	$\Delta h^3_{1/2}$
1	3084	4.918	1.7333	1.2942	-	2.18	2.25
2	1605.1	7.8297	1.1675	0.4683	-	1.69	1.83
3	1542.3	24.1451	3.6002	2.4442	-	1.92	3.21
4	1345.5	21.6215	3.2239	2.2932			
5	1283	20.5615	3.0661	1.2299			
6	1068	9.0599	1.1309	0.5419	-	1.08	1.17
7	972	6.5962	0.9835	0.3945	-	0.92	1.00

Internal standard ν, cm^{-1} : 1 – 2965; 2 – 934.4; 3 – 733

Table 2. Values of the calculated properties of the sample of tetryl from the IR spectrum, published in [4]

No.	ν , cm^{-1}	A_1	A_2	A_3	$\Delta h^1_{1/2}$	$\Delta h^2_{1/2}$	$\Delta h^3_{1/2}$
1	3450	1.819	2.3221	0.8738	2.86	10	3.48
2	3400	1.6958	2.1649	0.8147	2.88	10	3.48
3	3150	0.3221	0.4112	0.1547	-	-	-
4	3096.7	5.8845	7.5121	2.8268	0.64	2.25	0.78
5	1688.1	11.2233	14.3277	5.3915	0.64	2.25	0.78
6	1619.1	9.2319	31.4217	11.8357	1.28	4.13	1.44
7	1505	8.4867	10.834	4.0769	0.43		1.09
8	1421.4	17.865	22.8064	8.5821	1.21	4.25	0.68
9	1355.6	15.67	20.0043	7.5276	-	-	-
10	1163.5	4.2117	5.3766	2.0232	0.39	1.38	0.48
11	1000	5.92	7.5575	2.8439	0.30	1.06	0.37

Internal standard ν , cm^{-1} : 1 – 2918.33; 2 – 918; 3 – 698**Table 3.** Values of the calculated properties of the sample of tetryl from the IR spectrum, published in [5]

No.	ν , cm^{-1}	A_1	A_2	A_3	$\Delta h^1_{1/2}$	$\Delta h^2_{1/2}$	$\Delta h^3_{1/2}$
1	3570						
2	3166.6	2.2183	0.778	1.4822	-	1.02	-
3	1613	3.8067	1.3352	2.5436	-	1.37	-
4	1539	5.8844	2.0638	3.9317	-	-	-
5	1343	6.1903	2.1712	4.1361	-	-	-
6	1290	5.4853	1.9239	3.6650	-	-	-
7	1062	1.983	0.6955	1.325	-	1.77	-
8	962	2.0558	1.3143	1.2875	-	1.88	-
9	820	0.6240	0.2189	0.417	-	1.18	-
10	800	1.6899	0.5927	1.1291	-	0.82	-

Internal standard ν , cm^{-1} : 1 – 2920; 2 – 921; 3 – 723

The values of $\Delta\nu$ (Table 4), ΔA (Table 5) and $\Delta h^*_{1/2}$ (Table 6) were calculated from the values given in Table 6 in Part 1 and from the data in Tables 1, 2 and 3 given in this work.

Table 4. Comparison between the shifts ($\Delta\nu$) of the maxima of the IR spectrum of the sample obtained from acetone solutions of tetryl aged 50 years (0) and the IR spectra published in [2] (1), [4] (2) and [5] (3) for pure tetryl

No.	ν , cm^{-1}	$\Delta\nu_1$, cm^{-1}	$\Delta\nu_2$, cm^{-1}	$\Delta\nu_3$, cm^{-1}
1	3094.423	+10.4	-2.23	-
2	1610.852	+5.75	-8.25	-2.15
3	1537.231	-5.069	-	-1.769
4	1504.475	-	-0.525	-
5	1341.382	-4.118	-14.218	-1.618

From the results in Table 4, it was evident that ageing shifted the maxima to a smaller wave number, because the content of oxygen and nitrogen in the molecules of tetryl decreased. The biggest results were for $\Delta\nu_2$.

Table 5. Comparison between the differences of the absorbances (ΔA) of the maxima in IR spectrum made from acetone solutions of tetryl aged 50 years (0) and the IR spectra published in [2] (1), [4] (2) and [5] (3) for pure tetryl

N	ν , cm^{-1}	ΔA_1 0-1	ΔA_1 0-2	ΔA_1 0-3	ΔA_2 0-1	ΔA_2 0-2	ΔA_2 0-3	ΔA_3 0-1	ΔA_3 0-2	ΔA_3 0-3
1	3094.423	-3.568	-4.534	-	0.871	-0.432	-	+0.55	-1.98	-
2	1610.852	-	-7.176	-1.751	-	-30.11	-10.52	-	-10.55	-1.256
3	1537.231	-21.1	-	-2.834	-1.652	-	-0.116	-0.536	-	-2.023
4	1504.475	-	-7.891	-	-	-10.46	-	-	-3.711	-
5	1341.382	-19.45	-13.5	-4.021	-1.837	-18.62	-0.784	-0.934	-6.169	-2.777

It is evident that the values in Table 5 confirm the results in Table 4, because they show the decrease of the concentration of $-\text{NO}_2$ groups during ageing of tetryl.

Table 6. Comparison between the differences of the values of $\Delta h^*_{1/2}$ of the maxima in IR spectrum made from acetone solutions of tetryl aged 50 years (0) and the IR spectra published in [2] (1), [4] (2) and [5] (3) for pure tetryl

N	v, cm ⁻¹	$\Delta h^*_{1/2}$								
		1 0-1	1 0-2	1 0-3	2 0-1	2 0-2	2 0-3	3 0-1	3 0-2	3 0-3
1	3094.423	-	-1.76	-1.83	-	-0.52	-	-	-0.35	-
2	1610.852	-	-1.03	-	-	-3.08	-0.32	-	-0.19	-
3	1537.231	-	-1.4	-2.69	-	-	-	-	-	-
4	1504.475	-	-	-	-	-	-	-	-	-
5	1341.382	-	-	-	-	-	-	-	-	-

The values for $\Delta h^*_{1/2}$ in Table 6 are bigger in the maxima from the IR spectra of non-aged tetryl. It is known that the biggest values of $\Delta h^*_{1/2}$ are connected with H-bonds formation on the base of bigger number of conformations of the investigated molecules. In this way, the results from Table 6 confirm the conclusion for the decrease of H-bonds formation during ageing of tetryl on the base of the decrease of oxygen and nitrogen content. The results in Tables 4, 5 and 6 confirm the results in Table 7 in the end of Part 1.

Conclusion

The processes of ageing of tetryl and TD-50 connected with the decrease of oxygen and nitrogen contents in the molecules of these explosives can be shown with shifts (Δv), differences of the absorbances (ΔA) of the maxima in IR spectra, the values of $\Delta h^*_{1/2}$ of the maxima with changes in the bands for $-\text{NO}_2$ groups and with presence of bands in UV-VIS and FTIR spectra for products of ageing of the investigated materials.

References

- [1] Liou M.J., Lu M.C., Chen J.N., Oxidation of Explosives by Fenton and Photo-Fenton Processes, *Water Res.*, **2003**, 37, 3172-3179.
- [2] Fellows R.I., Harvey S.D., Cataldo D.A., *An Evaluation of the Environmental Fate and Behavior of Munitions Materiel (Tetryl and Polar Metabolites of TNT) in Soil and Plant Systems*, September 1993, Prepared for U.S. Army Medical Research

and Development Command under a Related Services Agreement with the U.S. Department of Energy, Contract DE-AC06-76RLO 1830, Pacific Northwest Laboratory.

- [3] Hutchinson C.D., Krishna Mohan V., Millar R.W., Aminotetryls: Synthesis, Spectral Characterization, Thermal Decomposition and Explosive Properties, *Propellants, Explos., Pyrotech.*, **1984**, 9,161-171.
- [4] Croom R., Ampbell Cl., Fisco W., Hogan V., Arc W.F., Campis J., Castorina T., *Qualification of Analytical Reference of Energetic Materials*, Memorandum Report, 12.03.1980, US Army Armament Research and Development Command, Dover, New Jersey.
- [5] Military specification MIL-T-339.
- [6] Ganev R., Glavchev I., Tzvetkoff T., Ivanova M., Totev T., Investigation of Long-Term Ageing of Single Base Propellants by IR Spectroscopy, *Journal of Explosives and Propellants*, R.O.C., **2004**, 20(1), 7-12.
- [7] Grozev V.I., Valchev V.P., Lazov N.K., Kazakov I.T., *Vzrivni veshtestva I baruti*, Izdatelstvo na MO "Sveti Georgi Pobedonosec", Sofia, **1997**, p.192 (in Bulgarian).