Spectroscopic Study of PVA-Glycerin-TPAH matrix with Nitroaromatic compounds: F-MOST a New Meisenheimer complex Effective Kit

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Abstract

The reaction between four tested nitroaromatic compounds with tetrapropyl ammonium hydroxide (TPAH) was used to produce Meisenheimer complex colour. This result was used to prepare a new fast, selective, and sensitive kit (F-MOST) composed of polyvinyl alcohol and glycerin beside the active agent (TPAH) with gel-like appearance. The gel-like appearance of F-MOST kit gave an advantage through excellent efficiency continued more than six months.

Keywords: nitroaromatic, tetrapropylammonium hydroxide, PVA, TNT, glycerin, gel like, kit.

Introduction

Meisenheimer reaction (Terrier, 1982) is Bimolecular Nucleophilic Aromatic substitution reaction occurs when a withdrawing group such as nitro attaches to aromatic ring reacts electron rich species (base) through elimination –addition mechanism results distinguished colour. This coloured anionic σ-adduct can be converted to a stable substituted complex as a result of Nitro –aromatic group presence.

Meisenheimer donor –acceptor intermediate application is famous with Nitroaromatic explosive materials (Al-Kaysi et al., 2004; Chen et al., 2004; Dasary et al., 2009; Liu et al, 2011; Hughes et al., 2015) such as 2,4,6-trinitrotoluene (TNT), picric acid, and 2,4,6-trinitrophenyl methyl nitroamine (Tetryl). The other application is reported in
orange – red colour formation of TNT- *Rhodococcus erythropolis* (Lenke and Knackmuss, 1992) by anionic σ-aromatic –hydride transfer.

The use of spectroscopic techniques in detection of nitroaromatic materials was in high position of concerns because of health and environment impacts especially that used as explosives in civil, commercial, military, and terrorist (Letzel et al., 2003; Dasary et al., 2014; Leffler et al., 2014). These techniques were fast, selective, sensitive, and with complicated instrumentations (Albert and Walt, 2000; Gallardo and Guirado, 2007; Fei et al., 2014). Many commercial kits were produced to detect nitro- and nitrate explosives in field or lab like EXPRAY®, E.L.I.T.E.™, LETK, DropEx plus, Gunshot, 3A3Z, … etc. depending upon known chemical reactions such as Meisenhemier and Griess reactions.

To take advantage of Meisenheimer reaction, in this paper we report the use of polyvinyl alcohol (PVA) and glycerin as a matrix (F-MOST) to hold the active agent tetrapropylammonium hydroxide (TPAH). To understand the selective TPAH-nitroaromatic complex formation, Ultraviolet – Visible (UV- VIS) and Fourier transform Infrared (FTIR) spectroscopies are used and further this gel – like (F-MOST) can be utilized for selective detection of nitroaromatic explosives including 2,4,6-trinitrotoluene (TNT).

**Experimental Section:**

**Materials**

Tetrapropyl ammonium hydroxide (C$_{12}$H$_{29}$NO), 4-Nitrophenol (slightly yellow crystal, C$_6$H$_5$NO$_3$), 4-Nitro-1,2-phenylenediamine (dark red needles, C$_6$H$_7$N$_3$O$_2$), 3-Nitroaniline (yellow crystal, C$_6$H$_6$N$_2$O$_2$) were manufactured by Merck Company. 2,4,6-Trinitrotoluene (TNT) (commercial yellow crystal, C$_7$H$_5$N$_3$O$_6$) was obtained from Iraqi Ministry of Interior as a sample under test qualified by FTIR and XRD instruments and their library search. All chemicals were used without further purification.

**Instruments**

FTIR (ABB Spectrolab HORIZON MB™, UK) and UV-VIS (UV-1650, Shimadzu, Japan) were used in this work to utilize both Infrared and Ultraviolet- Visible spectra for the prepared samples.

**Methods**

1 gm of polyvinyl alcohol (PVA), 2 gm glycerin, and 10 mL deionized water were mixed with accurate volume of tetrapropyl ammonium hydroxide (TPAH) (Table -1-) and heated with stirring at 90°C for 9 min. the resulted thick material (gel like, F-MOST) was left to cool to room temperature. 5 mg of the gel like was added to an accurate weight of each nitroaromatic compound and mixed. The resulted colored thick matrix was diluted with 5 mL of equal volumetric ratio water: ethanol solution
for UV-VIS measurements. Also before this step, the TPAH reagent (1 mg) was mixed with each nitroaromatic compound (1 mg) without the gel like matrix to qualify their maximum wavelength. (See Figures -1- and -2-)

Figure -1-: UV-VIS Spectra of each tested nitroaromatic compound and TPAH - gel like matrix.

Figure -2-: UV-VIS Spectra of each tested nitroaromatic compound and TPAH without gel like matrix.

Table -1-: Ultraviolet – Visible data of 3- Nitroaniline with F-MOST.

| Wt | Absorbance |
|----|------------|
|    |            |
| (3-Nitroaniline), mg | Vol. TPAH, mL | 325nm | 375 nm | 432 nm | 473 nm |
|----------------------|--------------|--------|--------|--------|--------|
| 0.1                  | 0.1          | 0.221  | 0.386  | 0.138  | 0.023  |
|                      | 0.5          | 0.959  | 1.498  | 0.601  | 0.159  |
|                      | 1            | 0.291  | 0.483  | 0.193  | 0.036  |
|                      | 2            | 0.107  | 0.126  | 0.054  | 0.011  |
| 0.5                  | 0.1          | 0.953  | 1.817  | 0.669  | 0.107  |
|                      | 0.5          | 0.761  | 1.279  | 0.490  | 0.093  |
|                      | 1            | 0.253  | 0.394  | 0.161  | 0.036  |
|                      | 2            | 0.357  | 0.579  | 0.234  | 0.045  |
| 1                    | 0.1          | 0.824  | 1.729  | 0.594  | 0.091  |
|                      | 0.5          | 0.914  | 1.624  | 0.651  | 0.155  |
|                      | 1            | 0.265  | 0.437  | 0.171  | 0.033  |
|                      | 2            | 0.419  | 0.671  | 0.282  | 0.057  |
| 2                    | 0.1          | 2.358  | 2.686  | 1.446  | 0.268  |
|                      | 0.5          | 0.940  | 1.500  | 0.597  | 0.154  |
|                      | 1            | 1.154  | 1.904  | 0.797  | 0.159  |
|                      | 2            | 2.146  | 2.395  | 1.909  | 1.642  |
| 3                    | 0.1          | 4.000  | 2.768  | 2.247  | 0.449  |
|                      | 0.5          | 0.920  | 1.516  | 0.577  | 0.110  |
|                      | 1            | 2.261  | 2.602  | 1.516  | 0.728  |
|                      | 2            | 0.232  | 0.348  | 0.149  | 0.029  |

Table -2-: Ultraviolet – Visible data of TNT with F-MOST.

| Wt (TNT), mg | Vol. TPAH, mL | Absorbance |
|--------------|---------------|------------|
|              |               | 325 nm     | 375 nm     | 432 nm     | 473 nm     |
| 0.1          | 0.1           | 0.177      | 0.156      | 0.151      | 0.151      |
|              | 0.5           | 0.086      | 0.053      | 0.040      | 0.034      |
|              | 1             | 1.168      | 1.144      | 1.151      | 1.149      |
|              | 2             | 0.127      | 0.095      | 0.082      | 0.076      |
| 0.5          | 0.1           | 1.165      | 1.010      | 1.319      | 1.420      |
|              | 0.5           | 1.738      | 1.517      | 2.142      | 2.474      |
|              | 1             | 0.244      | 0.195      | 0.311      | 0.384      |
|              | 2             | 0.244      | 0.195      | 0.311      | 0.384      |
| 1            | 0.1           | 0.970      | 0.806      | 1.134      | 1.307      |
|              | 0.5           | 1.521      | 1.299      | 1.888      | 2.232      |
|              | 1             | 1.528      | 1.495      | 1.539      | 1.571      |
|              | 2             | 0.271      | 0.164      | 0.261      | 0.327      |
| 2            | 0.1           | 1.026      | 0.889      | 1.489      | 1.774      |
|              | 0.5           | 1.021      | 0.890      | 1.385      | 1.636      |
Table -3-: Ultraviolet – Visible data of 4-Nitrophenol with F-MOST.

| Wt (TNT), mg | Vol. TPAH, mL | Absorbance |
|--------------|---------------|------------|
|              | 325 nm | 375 nm | 432 nm | 473 nm |
| 1            | 1.574  | 1.528  | 1.688  | 1.769  |
| 2            | 0.543  | 0.474  | 0.682  | 0.805  |
| 0.1          | 1.328  | 1.227  | 1.635  | 1.834  |
| 0.5          | 3.311  | 2.572  | 3.436  | 3.913  |
| 1            | 1.608  | 1.616  | 1.800  | 1.896  |
| 2            | 1.625  | 1.343  | 2.022  | 2.515  |

Table -4-: Ultraviolet – Visible data of 4-Nitro-1,2-phenylenediamine with F-MOST.

| Wt (4-Nitrophenol), mg | Vol. TPAH, mL | Absorbance |
|------------------------|---------------|------------|
|                        | 325 nm | 375 nm | 432 nm | 473 nm |
| 0.1                    | 0.138  | 1.301  | 1.093  | 0.021  |
| 0.5                    | 0.813  | 1.759  | 2.086  | 0.061  |
| 1                      | 0.512  | 1.187  | 3.311  | 0.587  |
| 2                      | 0.400  | 2.694  | 3.039  | 2.192  |
| 0.1                    | 0.190  | 1.787  | 1.518  | 0.028  |
| 0.5                    | 0.400  | 2.853  | 3.135  | 0.623  |
| 1                      | 0.3656 | 2.653  | 3.215  | 1.074  |
| 2                      | 0.400  | 2.834  | 3.135  | 2.860  |
| 0.1                    | 0.143  | 1.229  | 1.005  | 0.031  |
| 0.5                    | 0.383  | 0.714  | 0.839  | 0.320  |
| 1                      | 0.228  | 2.799  | 3.068  | 0.530  |
| 2                      | 0.400  | 3.135  | 2.860  | 2.515  |
| 2                      | 0.187  | 1.723  | 2.960  | 0.355  |
| 0.5                    | 0.583  | 2.723  | 2.893  | 0.098  |
| 1                      | 0.3957 | 2.853  | 3.135  | 3.374  |
| 2                      | 0.3913 | 3.817  | 3.010  | 0.591  |
| 0.1                    | 4.000  | 3.135  | 3.612  | 1.399  |
| 0.5                    | 4.000  | 2.783  | 2.985  | 0.401  |
| 1                      | 4.000  | 2.737  | 3.010  | 0.363  |
| 2                      | 3.957  | 3.039  | 3.436  | 1.251  |

Table -4-: Ultraviolet – Visible data of 4-Nitro-1,2-phenylenediamine with F-MOST.
Results and Discussion

Initially, this work was designed on oral thin film strategy with some modifications to obtain fast, sensitive, and selective identification of nitroaromatic compounds especially that used in explosion as a new kit we named it F-MOST. In this modified strategy we used polyvinyl alcohol (PVA) as a thick solution or gel like former and glycerin as a plasticizer. This PVA was reported with glycerin as oral thin film might be used as a drug releaser or carrier (Verma et al., 2015) therefore can release our newly applied Meisenheimer complex agent (TPAH) forming a coloured product.

Also, this combination (PVA, glycerin, and TPAH) was tested as a thin film-Meisenheimer complex agent with different nitroaromatic compounds and characterized with various spectroscopic techniques that will be published next time.

To characterize the formed thick solution produced from mixing and heating our previously mentioned combination at different times of heating and the produced colour of F-MOST with different NO₂ – compounds, FTIR and UV-VIS spectroscopies were used.

Fourier Transform Infrared spectroscopy (FTIR) is a good analytical technique employed in this work to determine the matrix and Meisenheimer complex functional groups by ABB FTIR. Several peaks were obtained using FTIR instrument.
representing different functional groups belong to the gel-like TPAH after different times of heating and mixing (75, 50, 40, or 9) min. (Figure-3). The broad peak at 3362 cm\(^{-1}\) represents O-H stretch of alcohol and hydroxide. The peak at 2942 cm\(^{-1}\) represents an aliphatic C-H while (1110 and 1044) cm\(^{-1}\) indicate C-O stretch in the gel-like TPAH matrix after 9 min. of mixing and heating. These observed peaks were repeated in other FTIR spectra after (75, 50, and 40) min. (Figure -3-) and with Meisenheimer complex formation (Figure -4-) with a little shifting in wave number. These noticeable results identify that F-MOST matrix did not affect by time of heating and the resulting matrix can be considered as a primary stable matrix.

Also, Figure -4- shows other peaks can be attributed to C=C (1642 cm\(^{-1}\)) symmetrical and (1522 cm\(^{-1}\)) non-symmetrical stretching vibration in the phenyl ring (aromatic system) beside the absence of -NO\(_2\) symmetrical stretching or its other vibrations. This -NO\(_2\) absence in FTIR spectra (Figure -4-) might be resulted from anionic complex formation (Equation -1-) nitrocyclohexyl dienyl anion system for all tested nitro compounds except TNT as trinitrocyclohexyl dienyl anion.

![](image)

\[ G: \text{functional group (NH}_2, \text{OH, CH}_3 \]
\[ n: 1 \text{ or } 3 \]
\[ \text{Nu: nucleophile or base.} \]

Equation 1: Anionic Meisenheimer complex formation.

The other identification technique in this work was UV-VIS spectroscopy that used to test the Meisenheimer complex formation without (Figure -1-) and with (PVA – glycerin) presence (Figure -2-). Tables (1 to 4) and Figures (-1- and -2-) show that different absorption peaks were appeared verifying the complex formation. The absorption maxima can be revealed to \(\pi\) electrons distributed over the aromatic ring. The variation of absorbance of these different formed complexes at the same tested conditions (weight of nitro-compound and volume of TPAH) caused by the substituent attached to the aromatic ring (methyl, hydroxyl, or amine).

Also, Figures (-1-, -2-, 5 to 8) and Tables (1-4) bring to light the effect of changing of TPAH and Nitro upon absorbance and finally the wise decision of using this gel-like as a identification kit of nitroaromatic explosives.

The increasing of nitro-weight caused the increasing of colour intensity while the increment of TPAH volume reduced colour intensity. The drooping in absorbance with basic Meisenheimer agent can be due to dilution effect where the required
quantity of TPAH was reacted with equal quantity of nitro compound producing the complex and the rest of TPAH might be acted as a diluted material.

Figure -3-: FTIR spectra of F-MOST gel-like matrix at different times of heating and mixing.

Figure -3-: FTIR spectra of F-MOST gel-like matrix at different times of heating and mixing.
Figure 4: FTIR spectra of Meisenheimer complexes of Nitroaromatics and F-MOST.

Figure 5: Reaction of TPAH and 3-Nitroaniline at 432 nm.

Figure 6: Reaction of TPAH and TNT at 432 nm.
Figure -7-: Reaction of TPAH and 4-Nitrophenol at 432 nm.

Figure -8-: Reaction of TPAH and 4-Nitrophenylenediamine at 432 nm.
Figure -9-: UV-VIS spectrum of TNT with F-MOST result after 58 days of preparation.

Our F-MOST efficiency was tested after (35, 58, and 135) days and gave an excellent result of colour intensity (UV-VIS measurement) and the easy of pushing out from the glue like tube (Figure -9-).

**Conclusion:**
In conclusion, the reaction between four tested nitroaromatic compounds with tetrapropyl ammonium hydroxide (TPAH) produced Meisenheimer complex colour. This result was used to prepare a new fast, selective, and sensitive kit (F-MOST) composed of polyvinyl alcohol and glycerin beside the active agent (TPAH) with gel like appearance. The gel-like appearance of F-MOST kit gave an advantage of producing it as glue-like tube with excellent efficiency continued more than six months with expectation of more.

**References**

1- Albert K. and Walt D. (2000). High speed fluorescence detection of explosive –like vapors. Anal. Chem 72, 1947-1955.
2- Al-Kaysi R., Creed D., and Valente E. (2004). Meisenheimer complex from picric acid and diisopropyl carbdiimide. J. Chem. Crystallogr. 34, 685-692.
3- Chen H., Chen H., and Cooks R. (2004). Meisenheimer complexes bonded at carbon and at oxygen. J. Am. Soc. Mass Spectr. 15, 998-1004.
4- Dasary S., Senapati D., Singh A., Anjaneyulu Y., Yu H., and Ray P. (2011). Highly sensitive and selective dynamic light –scattering assay for TNT detection using p- ATP attached gold nanoparticle. ACS Appl. Mater. Interface 2, 3455-3460.
5- Dasary S., Singh A., Senapati, Yu H., and Ray P. (2009). Gold nanoparticle based label-free SERS probe for ultrasensitive and selective detection of trinitrotoluene. J. Am. Chem. Soc. 131, 13806-13812.

6- Fei T., Jiang K., and Zhang T. (2014). Highly sensitive TNT photoluminescent sensing by a phosphorescent complex. Sens. Actuat. B Chem. 199, 148-153.

7- Gallardo I. and Guirado G. (2007). Electrochemical mechanism of spiro and zwitterionic Meisenheimer compounds: a potential fluorescence molecular switching system. Electrochem. Commun. 9, 173-179.

8- Hughes S., Dasary S., Begum S., Williams N., and Yu H. (2015). Meisenheimer complex between 2,4,6-trinitrotoluene and 3-aminopropyltriethoxysilane and its use for a paper-based sensor. Sens. Bio-Sens. Res. 5, 37-41.

9- Leffler P., Brannas E., Ragnvaldsson D., Wingfors H., and Berglind R. (2014). Toxicity and accumulation of trinitrotoluene (TNT) and its metabolites in Atlantic salmon alevins exposed to an industry polluted water. J. Toxicol. Environ. Health A. 77, 1183-1191.

10- Lenke H. and Knackmuss H. (1992). Initial hydrogenation during catabolism of picric acid by Rhodococcus erythropolis HL 24-2. Appl. Environ. Microbiol. 58, 2598-2606.

11- Letzel S., Goen T., Bader M., Angerer J., and Kraus T. (2003). Exposure to nitroaromatic explosives and health effects during disposal of military waste. Occup. Environ. Med. 60, 483-488.

12- Liu Y., Wang H., Indacochea J., and Wang M. (2011). A colorimetric sensor based on anodized aluminum oxide (AAO) substrate for the detection of nitroaromatics. Sens. Actuat. B. Chem. 160, 1149-1158.

13- Pesenti A. Taudte R., McCord B., Doble P., Roux C., and Blanes L. (2014). Coupling paper based microfluidics and lab on a chip technologies for confirmatory analysis of trinitroaromatic explosives. Anal. Chem. 86, 4707-4714.

14- Terrier F. (1982). Rate and Equilibrium studies in Jachson – Meisenheimer complexes. Chem. Rev. 82(2), 78-150.

15- Verma N., Singh S., Singh A., Rai P., and Singh R. (2015). Formulation, Optimization, and Evaluation of Fast Dissolving oral Film of Domperidone. J. Drug Discov. Therap. 3(32), 15-20.