Kinetic Spectrophotometric Determination of Propellant Grade Hydrazines using Thiophenes with Active Carbonyl Groups

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ABSTRACT

A simple, cost effective, highly sensitive and rapid kinetic spectrophotometric method was developed for hydrazines by using Thiophene-3-carboxaldehyde (3-Thienaldehyde) and 3-Butenone (E)-1,1,1-trifluoro-4-(3-thienyl) (CF_3 enone). CF_3 enone was prepared by crossed aldol condensation of 3-Thienaldehyde and characterized by UV-Vis, FT-IR and NMR spectra. Reactions of 3-Thienaldehyde (with catalyst) and CF_3 enone (in acetonitrile medium without catalyst) with hydrazines were followed spectrophotometrically and compared. Variables such as temperature and concentration were optimized to determine hydrazines in the concentration range of 0.1 mM to 0.1 M for 3-Thienaldehyde and 0.1 mM to 1 mM for CF_3 enone. Minimum detectable limits were found to be 0.2 mM (Hydrazine) and 0.1 mM (MMH) for 3-Thienaldehyde. For CF_3 enone, Minimum detectable limits were found to be 0.007 mM (Hydrazine) and 0.01 mM (MMH). Rate of the CF_3 enone reaction was studied as there is gradual decrease in absorbance for the peak at 320 nm for the interaction of hydrazines. Initial rate and fixed time methods were adopted for kinetic study. CF_3 enone based kinetic spectrophotometric method is rapid and sensitive with no catalyst requirement for interaction of hydrazines when compared with the classical CHO functional group based method.

Keywords: Kinetic spectrophotometric method, CF_3 enone, thiophene-3-carboxaldehyde, hydrazine, MMH

1. INTRODUCTION

Hydrazine and its derivatives are used as high energy propellants in space launch vehicles, satellites and aircraft emergency power units and as reactants in military fuel cells due to their highly reactive and reducing nature. Besides being reactive and explosive, they are known carcinogenic and neurotoxins[1]. In addition to their mutagenic nature, they have adverse health effects on brain and liver resulting in DNA damage. Due to their volatile and highly toxic nature, adverse health effects such as skin sensitization, eye irritation, thyroid amyloidosis, respiratory tract problems as well as systemic poisoning were observed on people working in such atmosphere. Even at very low levels of exposure, they exhibit toxic effects in humans. Hence, threshold limit values (TLV) for both hydrazine and monomethylhydrazine (MMH) have recently been lowered to 10 ppb for an 8 h exposure, corresponding to a dose of 80 ppb per h. To minimize the risk of exposure, monitoring of the working environments of such propellants is must to ensure that they are below their hazardous levels. Hydrazines ignite spontaneously without an external ignition source which may cause explosion. Before launching of rockets and missiles, there will be some key transfer operations of these liquid propellants from road tankers to storage tankers and to stage tanks that should be done meticulously without any leakage. Hence, detection of these vapors at an early stage is must. In such an atmosphere of propellant handling areas, highly sensitive and selective detection of hydrazine will be of more useful.

Several methods for the determination of hydrazines have been reported in the past. These mainly include spectrophotometric[2-4] and fluorescence methods[5,6] which are mainly based on aldehyde derivative reactions. Though they are highly selective, they are less sensitive and time-consuming. There is a need for catalyst for such type of reactions with pre-concentration step requirement. Kinetic methods are very simple, fast and low cost alternative methods as some of the experimental steps such as filtration, extraction, etc. can be avoided prior to absorbance measurements. They have high selectivity as they involve absorbance measurement as a function of reaction time instead of measuring the concrete absorbance value. Only a few kinetic spectrophotometric[7-9] and fluorescence methods[10] have been reported for the determination of trace level hydrazines. Such methods have been applied mainly to boiler feed water, natural water, urine and tablets.

Hence, 3-Butenone (E)-1,1,1-trifluoro-4-(3-thienyl) (CF_3 enone) was opted and synthesized for specific detection of hydrazines. Reaction of CF_3 enone with hydrazines leading to the formation of Pyrazoline is characteristic of hydrazines. In addition to this, a kinetic approach has been followed for determination of hydrazine concentrations in organic medium based on its reactivity with active carbonyl group (CF_3CO –

functional group coupled through double bond) at 3-position of thiophene moiety. This kinetic study was compared with a trivial derivatization technique which is based on the condensation of an aldehyde functional group at similar position of thiophene moiety. Based on these observations, we wish to report in this work, a new kinetic spectrophotometric method which is rapid and more sensitive one for hydrazines.

2. EXPERIMENT

2.1 Reagents

Thiophene-3-carboxaldehyde (3-Thienaldehyde), 1,1,1-trifluoroacetone were sourced from Sigma Aldrich, USA. Hydrazine (Purity: 99.8% by GC) and Monomethylhydrazine (Purity: 99.7% by GC) are of propellant grade. Other chemicals used in the synthesis and characterization were procured from Merck, India. Chemicals used for the spectroscopy studies were of AR grade unless otherwise specified and double distilled water was used throughout.

2.2 Preparation of Solutions for 3-Thienaldehyde Trials

From the stock solution of 3-Thienaldehyde (0.1 M) in acetonitrile, solutions with concentrations of 0.0001 M, 0.0002 M, 0.001 M, 0.002 M and 0.004 M were prepared. The prepared stock solution of 3-Thienaldehyde is stable for at least one week if it is kept at 5 °C under closed conditions. 0.01 M, 0.1 M and 1 M HCl solutions were prepared using AR grade concentrated Hydrochloric acid.

For both propellant grade Hydrazine and MMH, one molar stock solution in water was prepared. From each stock solution, solutions with concentrations of 0.1 mM, 0.2 mM, 0.5 mM, 1 mM, 5 mM, 0.001 M, 0.01 M, 0.05 M, 0.1 M were prepared. The standard test method for hydrazines in water (ASTM-D1385-07) was used to standardize the concentration of these solutions. Spectrophotometric measurements were carried out at 458 nm.

2.3 Preparation of Solutions for CF₃ Enone Trials

Solubility of CF3 enone and its interaction with hydrazines were carried out in acetonitrile medium (lowest UV cut off) which is an advantageous one for the molecules with λ_{max} in the UV region.

Solutions of CF₃ enone with concentrations of 0.05 mM, 0.1 mM and 0.15 mM were prepared in 25 ml volumetric flask with acetonitrile medium. These solutions of CF₃ enone are stable for at least one week if they are kept at 5 °C under closed conditions.

For both propellant grade Hydrazine and MMH, one molar stock solution in acetonitrile was prepared. From each stock solution, solutions with concentrations of 0.1 mM, 0.25 mM, 0.75 mM and 1 mM were prepared. The standard ASTM method (D1385-07) was used to standardize the concentration of these solutions. Spectrophotometric measurements were carried out at 462 nm.

2.4 Synthesis of 3-Butenone (E)-1,1,1-Trifluoro-4-(3-Thienyl)

Synthetic procedure adopted by Reddy[11], *et al*. has

been followed for the synthesis of CF₃ enone with slight modification. To a solution of 3-Thienaldehyde (5.6 g-0.05 mol) in dry benzene (25 ml) was added glacial acetic acid (1.0 ml) followed by piperidine (1.0 ml) under nitrogen atmosphere. Since competitive self-condensation of trifluoroacetone takes place, it is necessary to add five fold excess of trifluoroacetone (28 g - 0.25 mol) in five parts over a period of 5 min every time and stirred at RT for about 12 hours. Reaction was followed by TLC (Ethyl acetate: n-Hexane = 15:85). After completion of the reaction, reaction mixture was quenched with saturated ammonium chloride solution. To this, 75ml of benzene was added. The solution was washed with sodium bisulphite solution (5%) to remove unreacted 3-Thienaldehyde followed by water wash to neutral pH. Then, the reaction mixture was dried over sodium sulphate, filtered and concentrated under vacuum. Pure compound is eluted with n-Hexane containing 1% ethyl acetate. It is to be noted (from NMR spectra of CF₃ enone) that the vinylic fragments are in trans configuration[11].

Yield 52% ; ¹H NMR (CDCl₃) 7.9 (d, J =16, 1H), 7.8 (m, 1H-aromatic), 7.4 (m, 2H-aromatic), 6.8 (d, J=15.4, 1H); ¹³CNMR (CDCl₃) 180.5, 143.2, 137.1, 132.8, 127.9,125.2, 116.4; FT-IR (NaCl) 3109 cm⁻¹ (Aromatic-CH), 2923 cm⁻¹, 2854 cm⁻¹ (Aliphatic-CH), 1712 cm⁻¹ (>C=O), 1600 cm⁻¹ (Olefinic C=C)

2.5 Characterisation

FT-IR spectra of the samples were recorded on ABB MB 3000 Fourier transform infrared spectrometer by coating the sample on NaCl disc. NMR spectra were recorded using JEOL ECA 500 MHz high resolution liquid state NMR spectrometer. Spectrophotometric measurements were performed on a spectrophotometer (Techcomp-8500) with 1 cm quartz cells thermo stated by a thermostatic water bath (Shimadzu-TB 85) at RT, 40 °C and 50 °C. All the kinetic datas were obtained from the plots using the program Microcal Origin 7.0.

3. RESULTS AND DISCUSSION

3.1 Spectroscopy Study of Interaction of 3-Thienaldehyde with Hydrazines

3.1.1 Chemical Structure and Reaction Mechanism

Chemical Structures of 3-Thienaldehyde, Hydrazine and MMH are given in Fig. 1. Condensation of 3-Thienaldehyde with Hydrazine and MMH (in the presence of acid catalyst) results in a product known as hydrazone. In the case of unsubstituted hydrazine, two moles of aldehyde can react with one mole of hydrazine to form an azine (Aldazine). The reaction mechanism as shown in scheme 1 involves the nucleophilic addition of the nitrogen base, followed by the elimination of water.
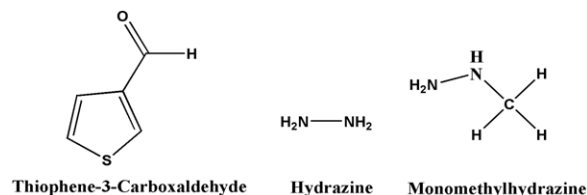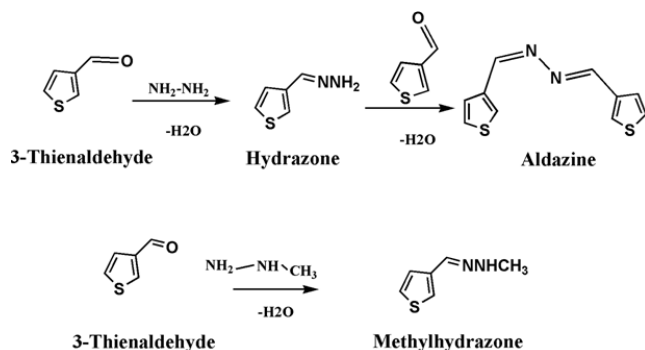

Figure 1. Chemical structures of 3-thienaldehyde, hydrazine and monomethylhydrazine.

Scheme 1. Interaction of 3-Thienaldehyde with Hydrazine and MMH.

3.1.2 Optimization of Variables

The reaction between 3-Thienaldehyde and hydrazines in the presence of HCl was followed spectrophotometrically by monitoring change in wavelength and absorbance. Preliminary experiments were performed to find the optimum test conditions and to study the influence of variables over rate of the reaction. Out of the various concentrations of 3-Thienaldehyde tried (0.0001 M to 0.004 M), 0.0002 M concentration was optimized for further studies. After fixing the concentration of 3-Thienaldehyde, concentration of hydrazines (Hydrazine and MMH) in the range of 0.1 mM to 0.1 M were tried in the presence of 0.1 M HCl solution which was an optimized one out of three concentrations (0.01 M, 0.1 M, and 1 M). Experiments were conducted on 3-Thienaldehyde in acetonitrile medium at RT, 40 °C and 50 °C to optimize the temperature for effective interaction. Difference in reactivity between 3-Thienaldehyde and hydrazines is marginal for the reactions carried out at 40 °C and 50 °C. For comparatively better reactivity, interaction at 50 °C was considered an optimized one.

Into a series of 5 ml volumetric flasks were added 2 ml of 3-Thienaldehyde of known concentration and 1 ml of 0.1 M HCl solution followed by 1 ml of Hydrazine solution (or MMH solution depending on the study requirement) in the increasing order of concentration. Aliquot of this reaction mixture is transferred to thermo stated 1 cm quartz cell against blank. Absorbance was measured for every 120 s during the first thirty minutes from the onset of the reaction. Changes in absorbance and wavelength were recorded with respect to time at room temperature (RT) and 50 °C. Disappearance of λ_{max} due to 3-Thienaldehyde (212 nm) and appearance of new maxima at higher wavelength due to azomethine link were observed and recorded in Table 1.

3.1.3 Hydrazine Interaction

For the addition of Hydrazine in the concentration range of 5 mM - 0.01 M at RT, λ_{max} of 232 nm was observed (Table 1) due to hydrazone formation[12] with no change in the absorbance values. On increasing the concentration from 0.01 to 0.05 M and above, there was further shift of 13 nm (from 232 nm). Here, notable change in absorbance was observed. For the addition of Hydrazine in the concentration range (5 mM to 0.01 M) at 50 °C, λ_{max} was red shifted by 10 nm (from 232 nm) with no change in absorbance. The red shift of λ_{max} in these cases was mainly due to extended conjugation as there is formation of Azine[13,14]. Observed values for λ_{max} (245 nm) and absorbance (1.29) were same for the addition of 0.05 M hydrazine at RT and 50 °C. This indicates the saturation level of Hydrazine at 0.05 M for the interaction with 3-Thienaldehyde. Out of Hydrazine concentrations (0.1, 0.2, 0.5, 1 mM) tried, 0.2 mM was practically found to be minimum detectable limit (MDL).

3.1.4 Monomethylhydrazine Interaction

Here, Procedure adopted for the reaction of 3-Thienaldehyde with Hydrazine was followed by replacing Hydrazine with MMH and the observations were recorded in Table 1. After fixing the concentration of 0.0002 M for 3-Thienaldehyde, addition of MMH in the concentration range (0.1 mM to 0.1 M) was tried in the presence of 0.1 M HCl.

For the addition of MMH in the concentration range (5 mM to 0.05 M) at RT, λ_{max} of 228 nm (Table 1) was observed due to Methylhydrazone formation [12]. Here, there was no change in the absorbance values. For the addition of MMH in the concentration range (5 mM to 0.1 M) at 50 °C, λ_{max} was red shifted by 23 nm (from 228 nm). Increase in absorbance value was also observed in these cases. Inductive effect of methyl group of methylhydrazone might be the reason for such changes[12]. Increase in temperature increases the rate of the reaction and hence increase in wavelength and absorbance. On increasing the concentration from 0.05 to 0.1 M at RT, red shift of λ_{max} by 15 nm (from 228 nm) was observed which might be due to increase in reactivity at high concentration. Out of MMH concentrations (0.1 mM, 0.2 mM, 0.5, 1 mM) tried, 0.1 mM was practically found to be MDL. It is apparent from Tables 1 that concentration of 0.05 M Hydrazine was sufficient to obtain Aldazine (245 nm; A=1.292) whereas 0.1 M concentration of MMH was required to obtain the same (243 nm; A=1.167). Due to unsubstituted nature of hydrazine, there is a possibility of forming two –CH=N- linkages which leads to extended conjugation. Hence, minimum concentration

Table 1 . Effect of concentrations of Hydrazine and MMH over the reaction with 3-thienaldehyde (0.0002 M)

Concentration (M)	Hydrazine				MMH			
	RT		50 °C		RT		50 °C	
	λ_{max} (nm)	A (a.u.)	λ_{max} (nm)	A (a.u.)	λ_{max} (nm)	A (a.u.)	λ_{max} (nm)	A (a.u.)
0.0005	232	1.054	241	1.026	228	0.938	250	1.117
0.001	232	1.056	243	1.075	230	0.937	251	1.104
0.01	232	1.096	241	1.045	228	0.968	251	1.103
0.05	245	1.292	246	1.285	228	0.957	251	1.145
0.1	245	1.287	248	1.294	243	1.167	250	1.153

of Hydrazine (0.05 M) was sufficient to reach 245 nm when compared with MMH.

3.2 Spectroscopy Study of CF_3 Enone and Hydrazines

3.2.1 Chemical Structure and Reaction mechanism

Chemical structure of CF_3 enone is given in Fig 2. The molar absorptivity (ε) of CF_3 enone solution (in acetonitrile medium) was found to be 1.9×10^4 dm^3 mol^{-1} cm^{-1}.

CF_3 enone in acetonitrile shows three peak maximas as shown in Fig. 4 (201 nm, 229 nm, 320 nm). While 201 nm is attributed to π- π* transition, 229 nm is attributed to n- π* transition and 320 nm is due to intramolecular charge transfer.

Reaction of trifluoroacetyl group with hydrazine proceeds faster at RT due to its strong electron acceptor character. FTIR study of this interaction showed that there is a complete disappearance of carbonyl vibration at 1712 cm^{-1} and C=C bond vibration at 1600 cm^{-1} followed by the appearance of C=N bond vibration at 1668 cm^{-1} (Fig. 3).
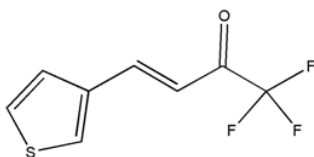

Figure 2. Chemical structure of CF_3 enone.

UV-Vis study of this interaction in acetonitrile medium (Fig. 4) showed that there is a decrease in absorbance for the peak at 320 nm which is followed by the formation of new peak at lower wavelength (232 nm). Decrease in absorbance for the peak at 320 nm is indicative of involvement of double bond and carbonyl group in the reaction leading to disturbance of the conjugation in the side chain of thiophene moiety and hence pyrazoline formation [11,15]. Due to hydrazine interaction, wave length at 229 nm is shifted to higher wavelength (232 nm). Pyrazolidine derivative of CF_3 enone is initially formed as intermediate in this interaction. This intermediate is transformed into pyrazoline (with C=N bond) by spontaneous elimination of water molecule as shown in the scheme 2. Hence, transformation[15] of pyrazolidine to pyrazoline might
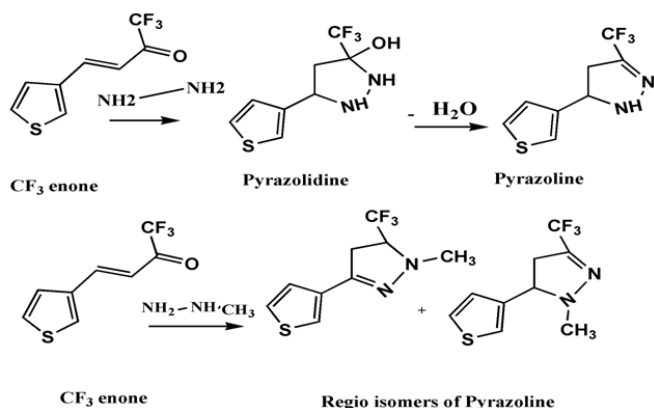
Scheme 2. Interaction of CF_3 enone with Hydrazine and MMH.

be the reason for such shifting. Similar pattern of change was observed for MMH interaction when studied by UV-Vis and FTIR (Fig. 3).

Similar nucleophilicity of the two nucleophilic centers of Hydrazine was cited by Nenajdenko[15], et al. as the reason behind the possibility of attack of the nucleophile at both the double bond and the carbonyl group. Due to methyl group substitution of MMH, two regioisomers of pyrazoline were expected to be formed[15].
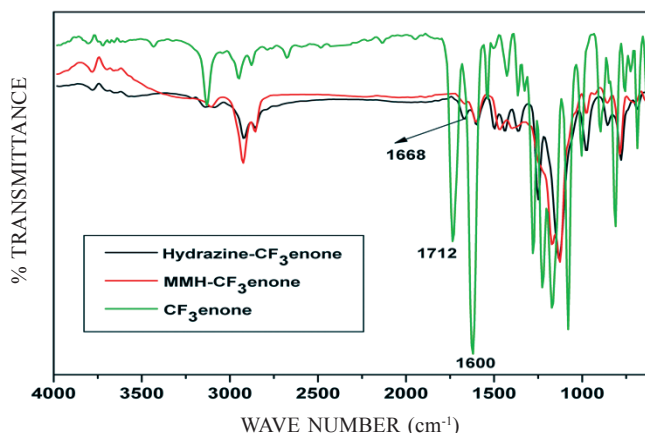

Figure 3. FTIR spectra - interactions of CF_3 enone with hydrazine and MMH.
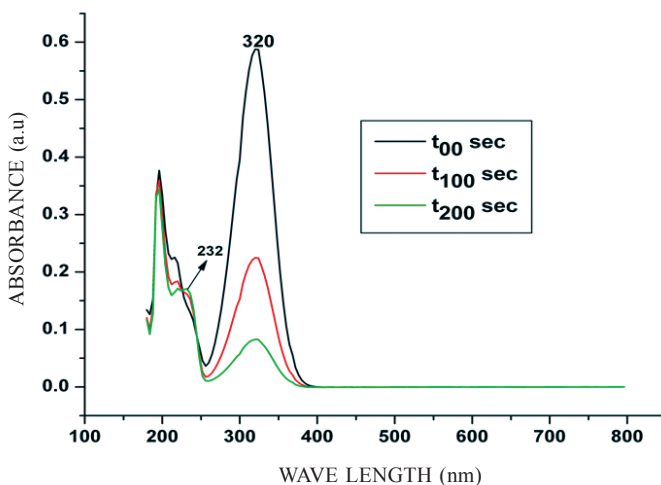

Figure 4. UV-Vis spectra - interaction of CF_3 enone with hydrazine.

### 3.2.2 Optimization of Variables

The reaction between hydrazines and CF_3 enone in acetonitrile medium was followed spectrophotometrically by measuring the decrease in absorbance of the peak at 320 nm as a function of time. Experiments were performed to optimize test conditions and to study the influence of concentration of hydrazines and temperature over the rate of the reaction. It is to be noted that moisture condition is to be avoided as water is reactive with $COCF_3$ functional group. Out of the various concentrations of CF_3 enone tried (0.05 mM, 0.1 mM and 0.15 mM), 0.05 mM concentration was optimized for further studies. After fixing the concentration to 0.05 mM, concentration in the range of 0.1 mM to 1 mM for Hydrazine

(or MMH depending on the study requirement) was tried at RT, 40 °C and 50 °C. Sensing study in the lower concentration range of analyte is pre-requisite for any sensing trials. Hence, lower concentration range (0.1 mM to 1 mM) was taken up for study.

CF$_3$ enone of known concentration and Hydrazine solution (or MMH solution depending on the study requirement) were added in 1:1 ratio into 5 ml volumetric flasks. Aliquot of this reaction mixture is transferred immediately into thermo stated 1 cm quartz cell against blank. Absorbance was measured for every 60 seconds during the first thirty minutes from the onset of the reaction. Absorbance variation of the peak at 320 nm was measured with respect to time at RT, 40 °C and 50 °C.
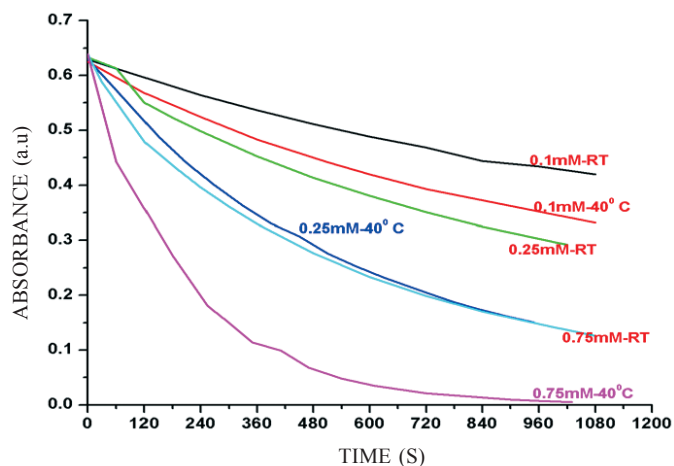
3.2.3 Effect of Concentration and Temperature

Effect of concentration of Hydrazine and temperature over the rate of the reaction of CF$_3$ enone was shown in Fig. 5. Influence of concentration of MMH and temperature over the reaction of CF$_3$ enone was shown in Fig. 6. Increase in ΔA (Decrease in absorbance) was observed on increasing the concentration of hydrazines and temperature (to 50 °C). Reactivity difference between Hydrazine and MMH with CF$_3$ enone was very much obvious from the Figs. 5 and 6. Reactivity of Hydrazine and MMH with CF$_3$ enone was greatly enhanced when the temperature is raised to 40 °C (from RT). Difference in the rates of reactions of MMH (for the addition of 0.1 mM, 0.25 mM and 0.75 mM) was only marginal on increasing the temperature from 40 °C to 50 °C. Hence, data was not produced.
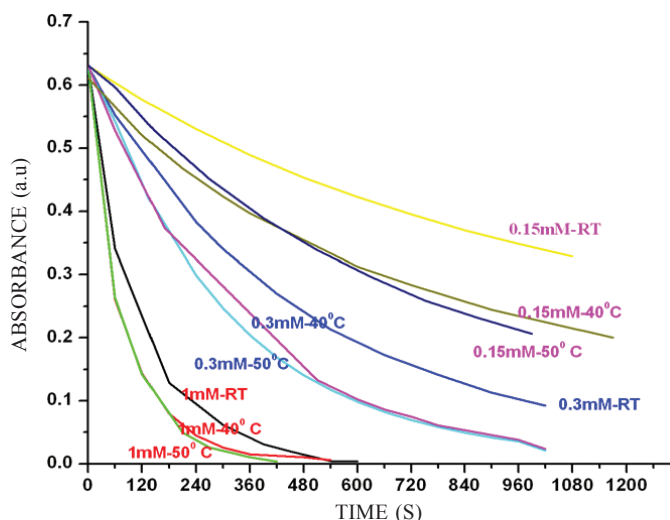
**Figure 5. Effects of Hydrazine concentration and temperature over CF$_3$ enone.**

In order to find the order of the reaction, rate of the reaction was found by systematically varying the concentrations of Hydrazine and CF$_3$ enone at RT. The order of the reaction was found to be two. (one with respect to CF$_3$ enone and the other one with respect to added hydrazine) (Table 2) Here, 6 min. was fixed while finding the order of the reactions. Similar type of change (second order) was observed while studying the rate of the reaction with MMH. Hence, data was not shown separately. MDL for Hydrazine was practically found to be 0.007 mM (shown in Fig. 7) and it was 0.01 mM for MMH (Fig. not shown)

Figure 6. Effects of MMH concentration and temperature over CF$_3$ enone.

Table 2. Effect of concentrations of CF$_3$ enone and Hydrazine over reaction rate

Concentration of CF$_3$ enone (mM)	Concentration of Hydrazine (mM)	Slope
0.05	0.30	-0.0010
0.1	0.30	-0.0018
0.15	0.30	-0.0033
0.05	0.15	-0.0004
0.05	0.30	-0.0010
0.05	1.00	-0.0014
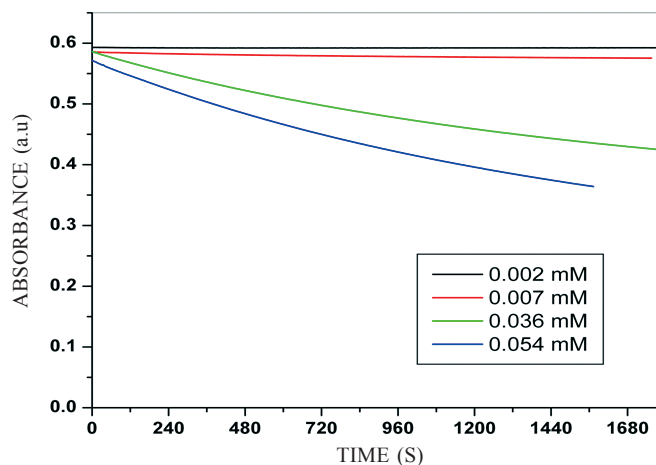
Figure 7. Trials done to find practical MDL for hydrazine.

3.3 Kinetic Study

The fixed time and initial rate methods were adopted for constructing the calibration curves.

3.3.1 Fixed Time Method
3.3.1.1 Hydrazine Interaction

In this method, decrease in absorbance of a solution (at λ$_{max}$ = 320 nm) was recorded till a preselected fixed time at RT, 40 °C, 50 °C. Out of three concentrations (0.15 mM, 0.3 mM, 1 mM) tried, rate of the reaction was higher for the addition of 1 mM hydrazine and the reaction was completed within 10 min. Hence change in absorbance was studied for the

fixed times of 3 min, 6 min, and 8 min. Calibration graphs were plotted at fixed times of 6 min, 8 min, 12 min, and 16 min for the trials with 0.15 and 0.3 mM hydrazine concentrations due to comparatively slow reaction. It is apparent from the values of slope and correlation coefficient (Table 3) that best linearity fit was observed for the first 6 min. Based on this study, 6 min was considered for initial rate method.

3.3.1.2 Monomethylhydrazine interaction

Decrease in absorbance of a solution (at λ_{max} = 320 nm) was recorded for the fixed times of 6 min, 8 min, 12 min, and 16 min for the addition of 0.1 mM, 0.25 mM, and 0.75 mM concentrations of MMH. Best linearity fit was observed for the first 6 min (Table 3). Hence, initial rate method was studied for 6 min.

3.3.2 Initial Rate Method

Under the optimized experimental conditions, initial rate of reaction was obtained by measuring the slopes (tan α = dA/dt) of the initial tangent to the absorbance-time curves with different concentrations of Hydrazine at different temperatures.

3.3.2.1 Hydrazine interaction

Data obtained from absorbance-time curve for different concentrations of Hydrazine at different temperatures by initial rate method (rate of reaction followed for first 6 min) are recorded in Table 4. By increasing the temperature from RT to 40 °C, increase in the rates of the reaction were found to be half fold for the addition of 0.3 mM hydrazine and two fold for addition of 0.15 mM Hydrazine. On increasing the

Table 3. Statistical data obtained from fixed time method

Hydrazine interaction

Parameter (min)	RT		40 °C		50 °C	
	Slope	R	Slope	R	Slope	R
1 mM						
3	-0.0027	-0.9619	-0.0030	-0.9280	-0.0026	-0.9135
6	-0.0014	-0.9094	-0.0014	-0.8478	-0.0015	-0.8544
8	-0.0010	-0.8798	-0.0008	-0.7623	--	--
0.30 mM						
6	-0.0010	-0.9977	-0.0014	-0.9971	-0.0015	-0.9987
8	-0.0008	-0.9883	-0.0010	-0.9819	-0.0010	-0.9825
12	-0.0007	-0.9767	-0.0008	0.9562	-0.0008	-0.9784
16	-0.0005	-0.9601	-0.0006	-0.9224	-0.0006	-0.9550
0.15 mM						
6	-0.0004	-0.9992	0.0007	-0.9945	0.0007	-0.9988
8	-0.0004	-0.9968	-0.0006	-0.9957	-0.0006	-0.9939
12	-0.0003	-0.9932	-0.0004	-0.9809	-0.0005	-0.9919
16	-0.0003	-0.9892	-0.0004	-0.9760	-0.0004	-0.9813

MMH interaction

Parameter (min)	RT		40 °C	
	Slope	R	Slope	R
0.75 mM				
6	-0.0008	-0.9815	-0.0014	-0.9738
8	-0.0007	-0.9744	-0.0012	-0.9510
12	-0.0006	-0.9642	-0.0008	-0.8982
16	-0.0004	-0.9522	-0.0005	-0.8353
0.25 mM				
6	-0.0005	-0.9826	-0.0008	-0.9942
8	-0.0005	-0.9827	-0.0007	-0.9889
12	-0.0004	-0.9817	-0.0006	-0.9808
16	-0.0003	-0.9776	-0.0005	-0.9684
0.10 mM				
6	-0.0003	-0.9992	0.0004	-0.9969
8	-0.0003	-0.9981	-0.0004	-0.9946
12	-0.0002	-0.9956	-0.0003	-0.9921
16	-0.0002	-0.9929	-0.0003	-0.9806

Table 4. Statistical data obtained from initial rate method

Hydrazine interaction

Concentration (mM)	RT		40 °C		50 °C	
	Slope	R	Slope	R	Slope	R
0.15	-0.0004	-0.9992	- 0.0007	-0.9945	-0.0007	-0.9988
0.3	-0.0010	-0.9977	-0.0014	-0.9971	-0.0015	-0.9987
1	-0.0014	-0.9094	-0.0014	-0.8478	-0.0015	-0.8544

MMH interaction

Concentration (mM)	RT		40 °C	
	Slope	R	Slope	R
0.10	-0.0003	-0.9992	-0.0004	-0.9969
0.25	-0.0005	-0.9826	-0.0008	-0.9942
0.75	-0.0008	-0.9815	-0.0014	-0.9738

temperature from 40 °C to 50 °C, slight variation in the rates for the addition of all the three concentrations (0.15 mM, 0.3 mM, 1 mM) was observed. No much variation in the rates of the reactions carried out at RT, 40 °C and 50 °C was observed while using 0.1 mM Hydrazine. While analyzing correlation coefficient values, linearity decreases while increasing the temperature and concentration to their higher values.

3.3.2.2 Monomethylhydrazine interaction

Data obtained from Absorbance-Time curve for different concentrations of MMH at RT and 40 °C by initial rate method are recorded in Table 4. It was observed that the rate of the reaction was higher and the reaction was near to completion within 16 min when 0.75 mM MMH was used. By increasing the temperature from RT to 40 °C, increase in the rates of the reaction were found to be two fold for the addition of 0.75 and 0.25 mM MMH. For the addition of 0.1 mM MMH, there was change in rate neither at RT nor at 40 °C. While analyzing correlation coefficient values, linearity decreases while increasing the temperature and concentration to their higher values.

4. CONCLUSIONS

The kinetic spectrophotometric method developed by us is quite simple, rapid and more sensitive than any other kinetic methods reported. This method can be used to determine hydrazine selectively at levels as low as 0.007 mM without the need for any pretreatment, pre concentration or extraction procedures. This method has an advantage of linear dynamic range at very low concentrations. When compared with the classical CHO functional group based method, kinetic spectrometry method developed by us have the following advantages
(a) There is no catalyst requirement such as concentrated strong acids
(b) Less concentration of CF_3 enone (0.05 mM) is sufficient
(c) Shortened analysis time (10 min for Hydrazine; 20 min for MMH).

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