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Spectrochimica Acta Part A 64 (2006) 93–100
SPECTROCHIMICA ACTA PART A
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Background defining during the imine formation reaction in FT-IR liquid cell

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Received 25 April 2005; received in revised form 1 July 2005; accepted 2 July 2005

Abstract

Imine formation is a very important chemical reaction because of its relevance to biological process. Therefore, it is crucial to follow whole reaction process in detail. The current work performed to monitor the whole imination reaction in real time in liquid cell by FT-IR spectroscopy. The complex spectral futures due to solvent, unreacted reagents, acid catalysis and other additives are eliminated by defining a background at the beginning or at any time during the reaction. This procedure also makes it possible to monitor the changes in the concentration of each component in the liquid cell. The consumption of the functional groups of the reagents results in absorbance due to the direct difference spectra while the appearance of functional groups is monitored as percentage transmittance. The concentration changes in the cell arising from the reaction gives the product spectra without having to isolate it from the mixture. It is also possible to see the intermediates appearing and disappearing during the reaction. This report also illustrates a brief application of the technique by time dependence of the peak highs in absorption (ABS) mode.

Keywords: Background defining; In situ time-dependent FT-IR; Imine formation

1. Introduction

Recent developments gave the scientist an opportunity to follow the reaction in situ by FT-IR [1] and Raman [2] spectroscopy. Because of the FT techniques it is quite practical obtaining a spectrum, which allows the scientist to have the spectra in the liquid or gas phase consecutively at different temperatures [3]. Liquid flow measurements were also conducted to observe all stages of the reaction [4]. The main problem of the interpretation on the IR spectra comes from method itself.

To eliminate the peaks due to the background material, defining a background is an essential requirement for FT-IR measurements. The background could be potassium bromide (KBr) disc for solid samples or pure solvent for liquid cells. In the case of mixed solvents, the solvent mixture can be employed as background. In this report we tried to define a new background, which is composed of both the reagent and the solvent. Having eliminated the absorptions due to the reagent and the solvent will give clearer spectrum containing FT-IR peaks only due to the products and intermediates.

Defining a background in such a way can be easily applicable even to the bimolecular reaction which has large molecular structure and quite difficult to distinguish each peaks [5].

We choose imine formation reaction between benzaldehyde and aniline to investigate by background defining method. This reaction was already examined by Raman [6] and LI-Raman [7] spectroscopy. Furthermore, reactions of salicylaldehyde and 2-pyridinecarboxaldehyde with aniline were also investigated.

Intermediates [8] play a fundamental role in the final product of the chemical reaction. Often, these intermediates cannot be monitored in real time however sometimes they can be trapped or isolated, but this time their characterization is a very time consuming process.

FT-IR as a reaction monitor can recognize the formation of intermediates [9] as well as determine reduction of reactants and formation of products. In most cases, it is not feasible

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doi:10.1016/j.saa.2005.07.020

to remove aliquots of a reaction mixture for measurement. Currently, more sophisticated and costly methods [10] like Fiber Optic Probe system capillary glass tube and micromachined flow cell [11] is used to allow real-time monitoring of the reaction. Defining the background at any time of the reaction allow us to eliminate all the peaks arising from any component or even product formed till that time and let us to follow any changes after that time.

2. Experimental

2.1. Application of the background defining

FT-IR spectra were collected using Perkin-Elmer Model BX 1600 instrument using 0.015 mm path length liquid CaF_2 cell.

1. Equivalent concentration of aldehyde and aniline was prepared in chloroform and FT-IR spectra of each reagent were recorded for comparison.
2. The reagents were mixed and scanned in the CaF_2 liquid cell after stirring.
3. The scanned spectra of the mixture were accepted as a background for the latter real time scans.
4. FT-IR spectra were collected sequentially in an optimum time intervals that are determined by reaction rate.
5. The increasing and decreasing peaks were compared with the reagents and product.
6. The extra peaks appeared in the spectra were attributed to the possible intermediates or interactions.

Ethyl alcohol and chloroform were used as solvents. The changes in the C=O and C=N bonds were observed perfectly in both solvents. However, no change in the amine peak was observed in the EtOH due to intense OH. Chloroform gave better spectrum as solvent while reagents and product are more soluble and no limitation over 1250 cm^{-1}.

The imine formation reaction between benzaldehyde and aniline was investigated by defining the beginning of the reaction as background. Fig. 1 shows the FT-IR spectra of reagents, benzaldehyde and aniline, the solvent, chloroform, and reaction mixture, which is defined as a background.

From the background defined reaction mixture spectra (Fig. 1b) it is easy to identify the aldehyde and amine functional groups in the mixture. Characteristic benzaldehyde peaks appeared at 1702 cm^{-1} for carbonyl and 2741 and 2822 cm^{-1} for COH hydrogen (Fig. 1c) and characteristic aniline aromatic stretching appeared at 1619 cm^{-1} as well as $-NH_2$ hydrogen peaks at 3376 and 3453 cm^{-1} in the chloroform (Fig. 1d) were all observed in the background spectra (Fig. 1b).

First recorded spectrum is used as background and the relative intensities of the peaks were examined. Two cases are, starting from the first recorded spectra after the scan used as background, the changes in relative peak intensities are clearly observed, indicating that the reaction continuous in the cell. Two cases are realized in the spectra, where the relative percentage transmittance increases (over 100%) or decreases (under 100%) depending on the concentration of the materials in the solution. For instance, when we consider the most intense peaks, the C=O at 1702 which is exactly the same as benzaldehyde is going up with time while C=N at 1630 cm^{-1} going down because of the product imine formation (Fig. 2).

As expected, the increasing peaks exactly coincide with the reagents in the solvent, indicating a concentration decrease. On the other hand, the decreasing peaks, which are at the same frequency with the product, indicate formation of a new compound. Therefore, it is also possible to estimate the

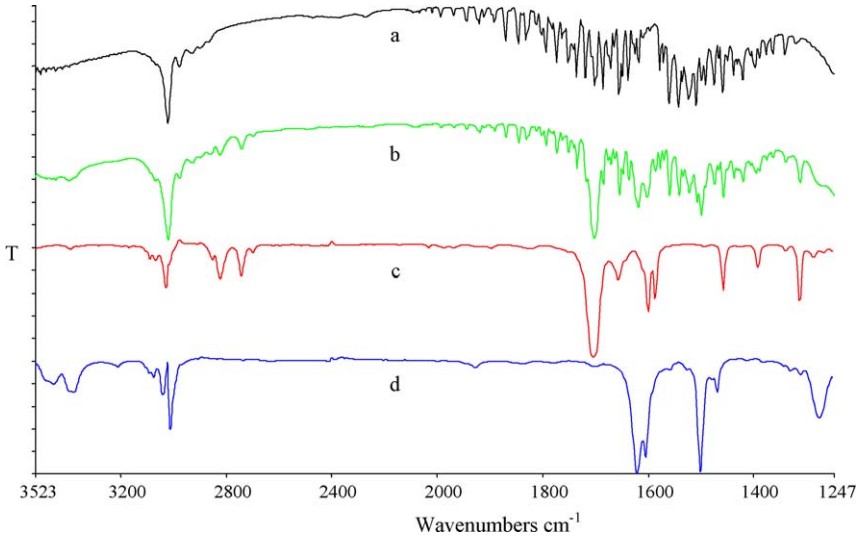


Fig. 1. FT-IR spectra of chloroform (a); background defined time of reaction mixture (b); benzaldehyde (c); aniline (d) (spectra were arbitrarily displaced in vertical for clarity).

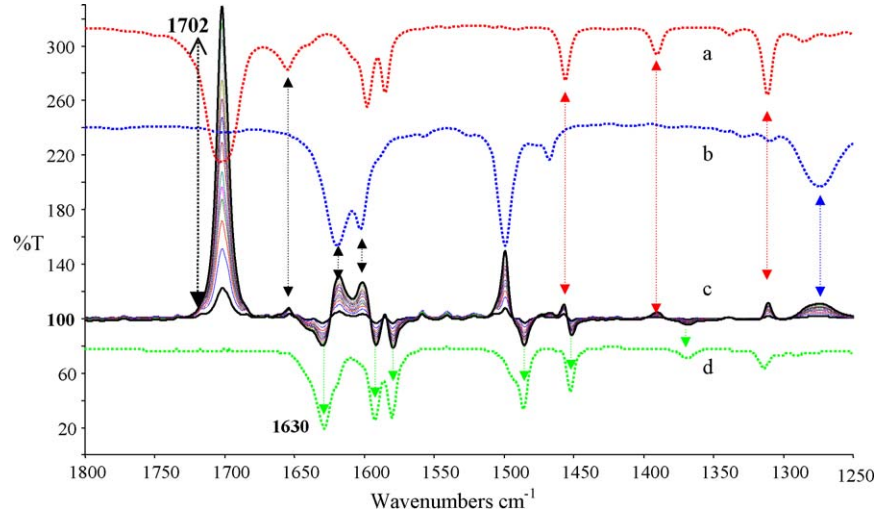


Fig. 2. Time resolved FT-IR spectra of the benzaldehyde and aniline in 1250–1800 cm^{-1} region (benzaldehyde (a), aniline (b), in situ real time scans of reaction mixture (c), isolated product (d)).

position of the increasing peaks from the pure benzaldehyde and aniline spectra in chloroform (Fig. 3).

In addition, by defining the background at any time of the reaction allows us to subtract the unreacted reagents and already formed products. This results in decreasing intensities of the peaks due to decreasing reaction rate. Because of the density differences of the chloroform and water, the formation of the water during the reaction do not disturb the FT-IR beam. Water related peaks have not been observed in the spectra (Fig. 4).

Consequent scanning of the reaction mixture after defining background gave more intense peaks by the time depended concentration changes. Fig. 5 shows the comparison of the FT-IR spectra of the reaction mixture with the reagents, benzaldehyde, aniline, and product, *N*-benzylideneaniline, in chloroform.

Considering negative peaks relative to 100% transmittance, it is possible to follow the product formation in solution starting from the beginning of the reaction without any interruptions of the other components. In order to validate the background defining method to other type of organic reactions, we applied the same analysis to the reactions of 2-salicylaldehyde (Fig. 6) and 2-pridinecarboxaldehyde (Fig. 7) with aniline (Scheme 1), both reactions gave similar observation with the benzaldehyde and aniline reaction, the positive peaks were appeared exactly at the same frequencies with the reagent while the negative with the isolated products in chloroform. However, the peak intensities and frequencies differ from each other. For instance, C=O peak appears at 1666, 1702 and 1714 cm^{-1} in 2-piridincarbaldehyde, benzaldehyde, and salicylaldehyde in chloroform, respectively. Similar differences on the products spectra for imine C=N

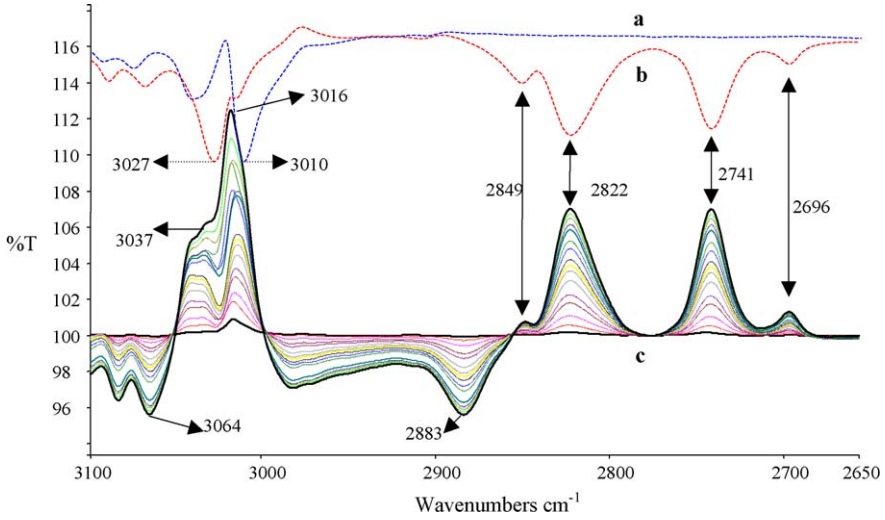


Fig. 3. Background defined baseline corrected FT-IR spectra of amine to the imines conversion 2650–3100 cm^{-1} (C—H) region (c) (the spectra of aniline (a) and benzaldehyde (b) were arbitrarily displaced in vertical for clarity).

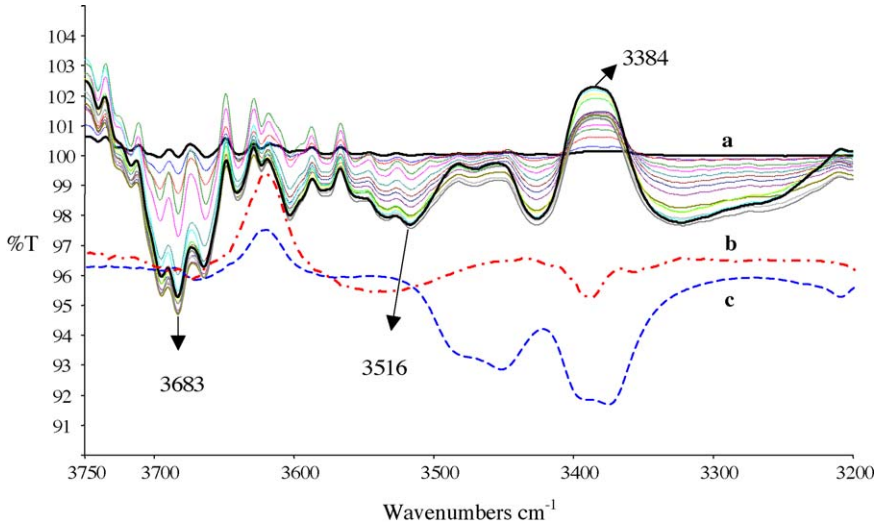


Fig. 4. Background defined baseline corrected FT-IR spectra of amine to the imines conversion 3200–3759 cm^{-1} region (a) (the spectra of benzaldehyde (b) and aniline (c) were arbitrarily displaced in vertical for clarity).

functionality at 1630, 1628, and 1620 cm^{-1} were also observed according to the aromatic ring (Figs. 5–7).

All reactions were slow enough to follow each step. Usually 5–20 min time intervals were used to observe significant changes. The rate of the reactions were considered according to the relative intensity changes on the background defined spectra and found that 2-pyridinecarboxaldehyde was faster than benzaldehyde while salicylaldehyde was slower.

2.2. *Comparison of the peak highs*

For a short application of the method, the reaction of benzaldehyde and aniline monitored for 90 min in a 3 min sequence. As soon as the same concentration of benzaldehyde and aniline (0.25 M) were mixed together, it was placed in to CaF_2 cell and scanned as background. After scanning the entire component in the cell as background, the solution was scanned in each 3 min and recorded for peak highs manipulation.

The peak highs for all the main peaks are obtained using the PE spectrum 2 in absorbance mode. The calculated values are shown in Table 1.

For the comparison of the peaks to each other, the other peaks values were plotted against the 1702 cm^{-1}. The good regressions for each line show that the peak highs may be used for latter calculation like concentrations.

The negative values arise from consumption of the reagent and positive values arise from appearance of the product. All the peak highs are related to the same concentration changes

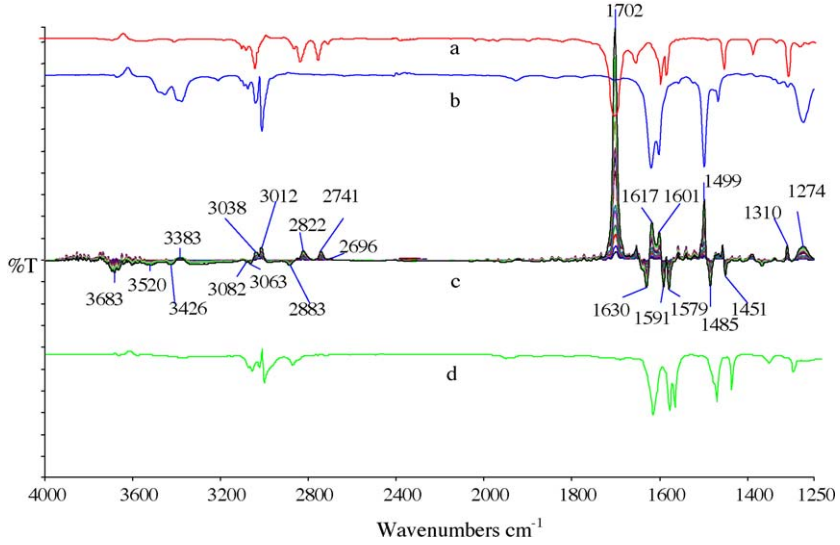


Fig. 5. FT-IR spectra of benzaldehyde (a); aniline (b); background defined in situ aniline and benzaldehyde reaction (c); isolated product in chloroform (d) (spectra of reagent and products were arbitrarily displaced in vertical for clarity).

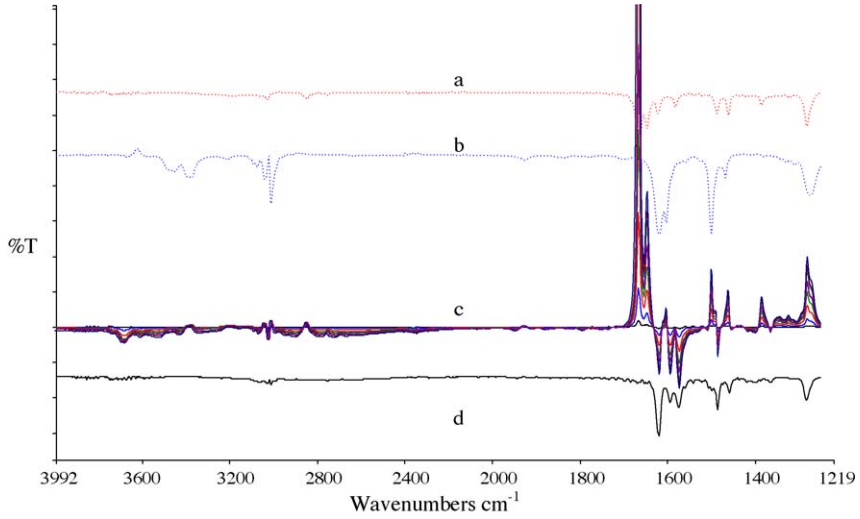


Fig. 6. FT-IR spectra of (a) salicylaldehyde (b) aniline (c) background defined reaction (d) isolated product (*N*-salicylideneaniline) in chloroform (spectra of reagent and products were arbitrarily displaced in vertical for clarity).

in the cell. So, calculating the concentration [*X*] at any time may give the directly product concentration and subtracting this value from the initial reactant concentration it is also possible to calculate the rest of the reactant concentration.

The time versus peak highs plots should give rough information about the rate of the reaction. As it is seen in Fig. 8 the increase or decrease on the line are not the same but related to the peak intensities for a single concentration by means of the most intense peak for C=O is the most lower value.

3. Results and discussion

Usually the observation of the reaction in the liquid cell was performed by addition of one of the reagent to the other and recording the changes [12]. However, liquid cell detection by this way is inconvenient for continuous monitoring of chemical reactions since each time a sample must be taken. Following each addition, the changes are very difficult to analyze and each time cleaning process of the cell by passing trough solvent and refilling for the next scan is necessary in order not to cause concentration differences. Subtracting the initial spectrums ($t = 0$) of reactants and solvent from latter may give some suggestion about the reaction but these subtraction may need tremendous work and subtracted spectra may not give valuable results for further studies [13]. This shortcoming can be overcome by continuous method by adding all the reagents at once and defining it a background. This allows us not to disturb the system until the end of the experiment (Fig. 9). In this work, an easy application of FT-IR spectroscopy for imine formation in a liquid cell was demonstrated. Analysis of the increasing and decreasing

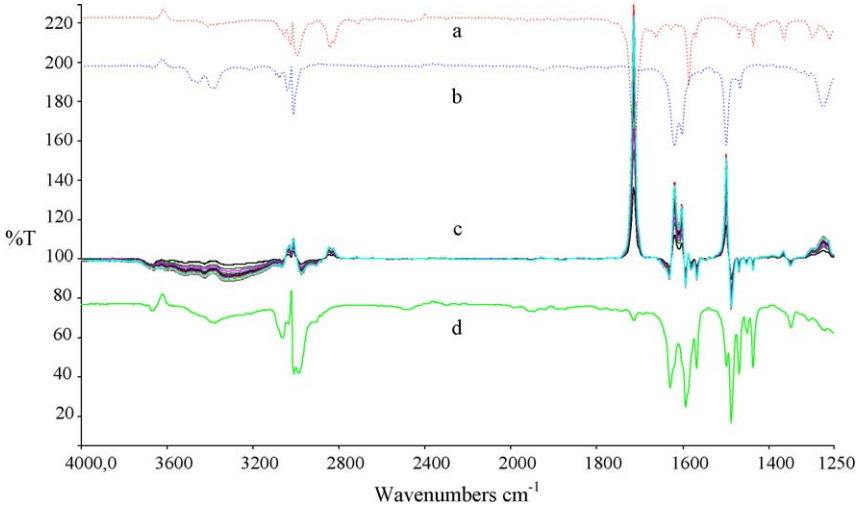
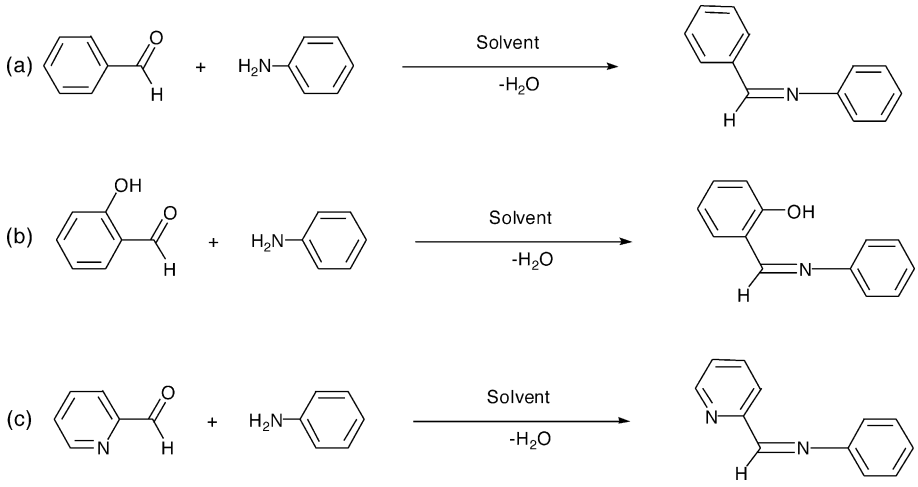


Fig. 7. FT-IR spectra of (a) 2-pyridinecarboxaldehyde, (b) aniline, (c) background defined real time scans and (d) isolated product in chloroform (spectra of reagent and products were arbitrarily displaced in vertical for clarity).

Table 1
The peaks height values (ABS) of in situ reaction of benzaldehyde and aniline in 3 min intervals

Time (min)	ABS								
	1702 (cm^{-1})	1629.9 (cm^{-1})	1618.1 (cm^{-1})	1601.3 (cm^{-1})	1591.7 (cm^{-1})	1579.5 (cm^{-1})	1499.4 (cm^{-1})	1485.5 (cm^{-1})	1451.5 (cm^{-1})
3	−0.0579	0.0099	−0.0136	−0.0099	0.0102	0.0109	−0.02	0.0095	0.0056
6	−0.1243	0.0223	−0.028	−0.0209	0.0225	0.0242	−0.0421	0.0213	0.0128
9	−0.1858	0.0338	−0.0412	−0.0321	0.0337	0.0367	−0.0626	0.0325	0.0196
12	−0.2333	0.0429	−0.0517	−0.0412	0.0424	0.0463	−0.0784	0.0412	0.0248
15	−0.2703	0.0499	−0.0597	−0.0485	0.0491	0.0539	−0.091	0.048	0.029
18	−0.2991	0.0557	−0.0659	−0.0542	0.0546	0.0601	−0.1005	0.0537	0.0324
21	−0.3214	0.06	−0.0706	−0.0589	0.0586	0.0647	−0.108	0.0579	0.0349
24	−0.3399	0.0636	−0.0747	−0.0629	0.0621	0.0686	−0.1141	0.0614	0.037
27	−0.3555	0.0666	−0.0782	−0.0662	0.065	0.0718	−0.1193	0.0643	0.0388
30	−0.3687	0.0692	−0.0811	−0.0691	0.0673	0.0746	−0.1238	0.0668	0.0403
33	−0.3802	0.0713	−0.0838	−0.0717	0.0693	0.0769	−0.1277	0.069	0.0415
36	−0.3904	0.0732	−0.0863	−0.0741	0.0711	0.0789	−0.1312	0.0707	0.0426
39	−0.3992	0.075	−0.0882	−0.076	0.0728	0.0808	−0.1341	0.0724	0.0436
42	−0.4075	0.0765	−0.0901	−0.078	0.0742	0.0824	−0.137	0.074	0.0445
45	−0.4146	0.0779	−0.0917	−0.0795	0.0755	0.084	−0.1393	0.0753	0.0454
48	−0.4215	0.0792	−0.0934	−0.0811	0.0767	0.084	−0.1417	0.0766	0.0461
51	−0.4278	0.0804	−0.0949	−0.0826	0.0779	0.0854	−0.1438	0.0778	0.0469
54	−0.434	0.0814	−0.0963	−0.084	0.0788	0.0867	−0.146	0.0788	0.0475
57	−0.4395	0.0825	−0.0976	−0.0853	0.0799	0.0878	−0.1477	0.0799	0.0481
60	−0.4446	0.0836	−0.0987	−0.0864	0.081	0.0891	−0.1493	0.081	0.0489
63	−0.4494	0.0845	−0.0998	−0.0876	0.0818	0.0903	−0.1509	0.082	0.0494
66	−0.454	0.0854	−0.1008	−0.0887	0.0827	0.0913	−0.1524	0.0829	0.0499
69	−0.4585	0.0862	−0.1018	−0.0897	0.0835	0.0923	−0.154	0.0837	0.0504
72	−0.4629	0.0871	−0.1028	−0.0908	0.0843	0.0932	−0.1554	0.0846	0.051
75	−0.4687	0.0876	−0.1047	−0.092	0.0849	0.0942	−0.1577	0.0849	0.0512
78	−0.4738	0.088	−0.1064	−0.093	0.0855	0.0948	−0.1596	0.0853	0.0513
81	−0.4783	0.0887	−0.1075	−0.0939	0.0862	0.0953	−0.1612	0.0859	0.0518
84	−0.4825	0.0895	−0.1085	−0.095	0.087	0.096	−0.1626	0.0868	0.0523
87	−0.4852	0.0901	−0.1091	−0.0957	0.0875	0.097	−0.1635	0.0874	0.0526
90	−0.4883	0.0907	−0.1097	−0.0965	0.088	0.0976	−0.1644	0.0881	0.0531



Scheme 1. Reactions of benzaldehyde (a), salicylaldehyde (b), 2-pyridinecarboxaldehyde (c), with aniline.

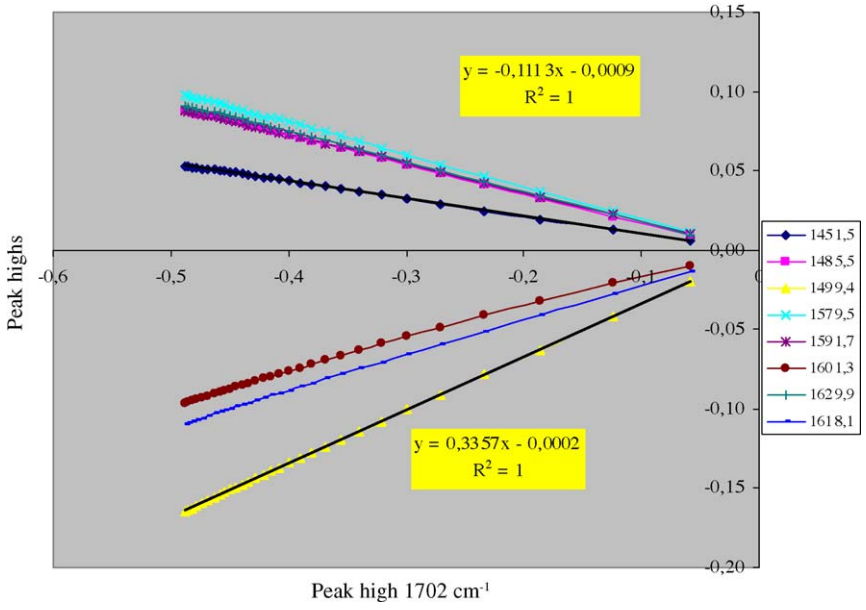


Fig. 8. The peak highs vs. 1702 cm^{-1} plots in 3 min intervals for overall 90 min.

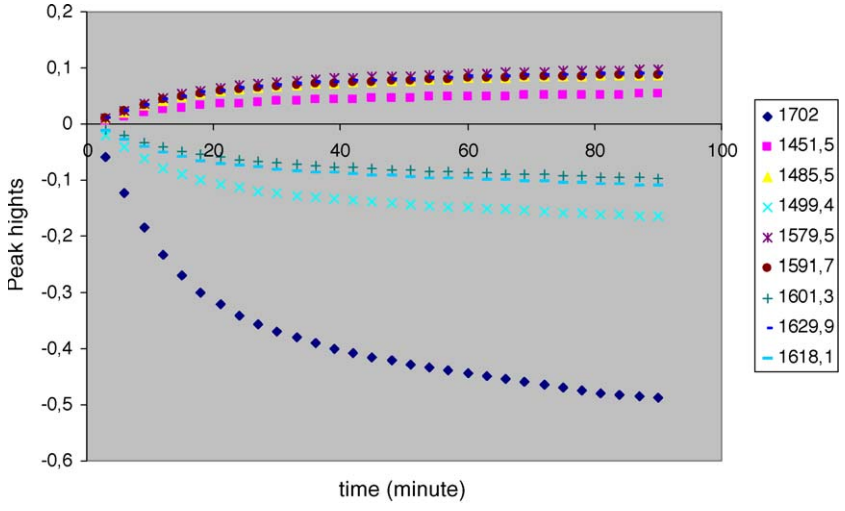
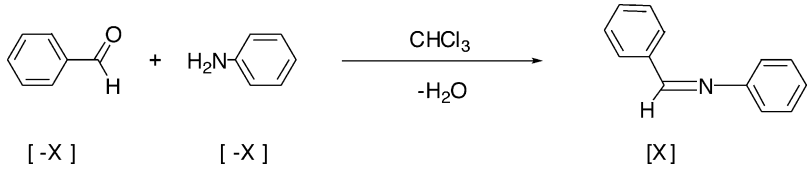


Fig. 9. Time to peak highs (ABS) plots of the benzaldehyde and aniline reaction.



Scheme 2. The concentration changes of the reaction that FT-IR recognizes.

peaks, after background subtraction were required in order to have an acceptable spectra from a small volume of chemical species in a liquid cell. As a result, a series of in situ real time direct difference FT-IR spectrum were accumulated for the imine formation reactions. We demonstrated the results of FT-IR detection of bond breaking and formation during the model reactions of imine formation in CaF_2 liquid cell. For an application the changes were scanned in each three min for overall 90 min. The peak highs in absorbance mode were calculated using the PE spectrum V2 software. The data were directly transferred to the MS excel for peak highs to peak highs and time to peak highs manipulations.

This study was carried out in order to establish an easy method of monitoring the organic reactions in situ by measuring the concentration changes during the reaction.

The decrease of the concentration of the reagents by reacting are appeared an upward peaks while the product formation downward peaks in transmittance mode. The decrease of the concentration by consumption cause to the less absorption bands conversely more transmittance (upward peaks) appearing on the same frequencies of the reagent in the solvent. The increase of the concentration of the product cause a new absorption bands (downward peaks). These all changes were attributed to the same concentration difference for the investigated reaction (Scheme 2).

4. Conclusion

FT-IR is a viable way of monitoring an organic reaction in real-time where there are recognizable differences in functional groups between reactants and the products. Defining the reactants and solvent mixture as a background at the beginning or at any time of the reaction makes the interpretation of changes more feasible. The product spectra may be obtained separately without isolating it from the reaction mixture due to the positive adsorption while reagents are negative.

The proposed method could also be applicable to the other accessories of the FT-IR, which would give an opportunity to follow any difference including the intermediates which are stable enough to scan by FT-IR.

The changes in concentration in the liquid cell were recognized by spectrophotometer and given as negative and positive peaks according to the consumption or formation. We have shown here an easy, inexpensive and simultaneous way to monitor the C=N bond formation and C=O and N–H bond breaking in real time in the CaF_2 liquid cell.

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