Heteroatom Chemistry
Volume 6, Number 2, 1995

Investigation of the Mechanism of Reaction of *S*-Ethyl-*N,N'*-tetraethyldiamidothiophosphite with $[C_5H_5Mn(CO)_2NO]^+BF_4^-$ by Fourier Transform Infrared Spectroscopy

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Received 19 July 1994; revised 27 October 1994

ABSTRACT

FT-IR spectroscopy and a special mathematical program were used for the real-time monitoring of the mechanistic path of the reaction of S-ethyl-N,N-tetraethyldiamidothiophosphite with $[CpMn(CO)_2NO]^+BF_4^-$. *The formation of a few intermediates is described.*

INTRODUCTION

The modern Fourier transform infrared (FTIR) technique proves to be very successful in investigations of the mechanism and kinetics of some reactions [1–4]. Use of this technique requires a thorough analysis of the analytical band intensities for each of the individual precursors and products. Unfortunately, it is very difficult to detect the bands belonging to intermediate products as most such bands have small intensities and can overlap with the bands of another compound. Such research requires a very careful experimental and theoretical approach and, therefore, the investigators must possess a sound mathematical background that makes realistic extension of experimental methods possible. For this purpose, the new spectral conversion program (CONVERSE) for the ASPECT-2000 software of the IFS-113V spectrometer has been set up. This makes it possible for us to plot, by use of an IBM PC, both a three-dimensional spectral surface (SS) (in the frequency-time-intensity axis) and its two-dimensional variant-isointensity lines in the frequency-time axis [spectral map (SM)]. The SM is very informative. If straight horizontal lines exist, there are no changes in the frequencies. On the contrary, any deviations from the horizontal lines or the appearance of cycles is indicative of a dynamic process. The SS and SM maps make it possible to observe features that do not appear by use of common techniques. The SM is very convenient for plotting kinetic curves at any frequency.

Recently [5], we have shown that the thioesters of P(III) acid derivatives, diamidothiophosphites in particular, react with cationic Mn complexes by substituting one CO group and forming stable cationic products having an Mn–P bond. In order to elucidate the mechanism of the reaction, we monitored the reaction of complex (**1**)

Dedicated to Professor Shigeru Oae on the occasion of his seventy-fifth birthday.

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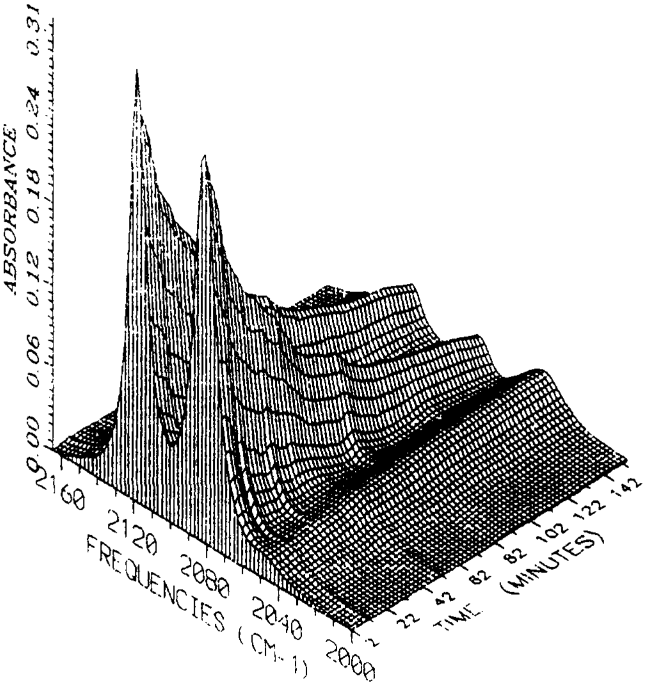


FIGURE 1 SS of the reaction mixture in the region of CO vibrations.

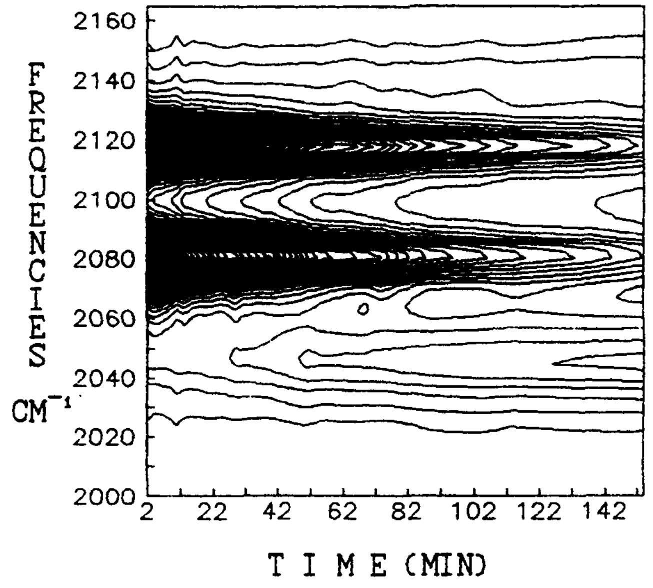
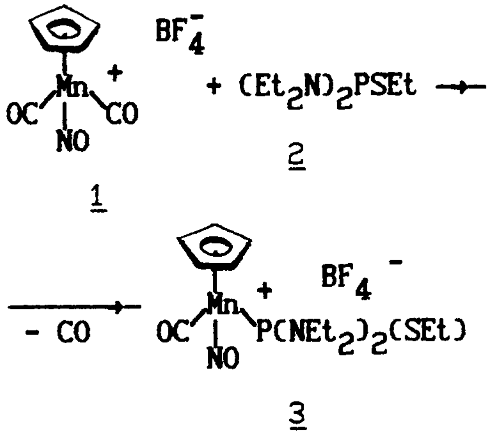


FIGURE 2 SM in the 2170–2000 cm^{-1} region during the first ~152 minutes of the reaction.



with *S*-ethyl-*N,N*-tetraethyldiamidothiophosphite (**2**) using FTIR spectroscopy.

RESULTS AND DISCUSSION

The IR spectra of the initial complex (**1**) are characterized by the absorption bands of the stretching vibrations *ν*(CO) at 2118 and 2082 cm^{-1} and *ν*(NO) near 1855 cm^{-1}. A distinctive feature of the spectra of product (**3**) is the appearance of the bands of the vibrations *ν*(CO) at 2039 cm^{-1} and *ν*(NO) near 1799 cm^{-1}. These spectral features were used for studying the reaction. In Figure 1, the SS in the 2170–2000 cm^{-1} region is given, in which intensities of the *ν*(CO) absorption bands were observed during the first 152 minutes of the reaction. The intensity of the 2118 and 2082 cm^{-1} bands from the doublet CO groups of the initial reagent (**1**) are decreasing, while the intensity of the 2039 cm^{-1} band of the product (**3**) is increasing. The same process can be observed in the SM map (Figure 2). Figure 3 presents part of the SS in the 1920–1679 cm^{-1} region recorded during the first 102 minutes. Figures 4 and 5 show the SM map of the same spectral region. It is quite simple to observe that the intensity of the band *ν*(NO) ~ 1855 cm^{-1} for compound (**1**) decreases, while the *ν*(NO) ~ 1799 cm^{-1} band for the

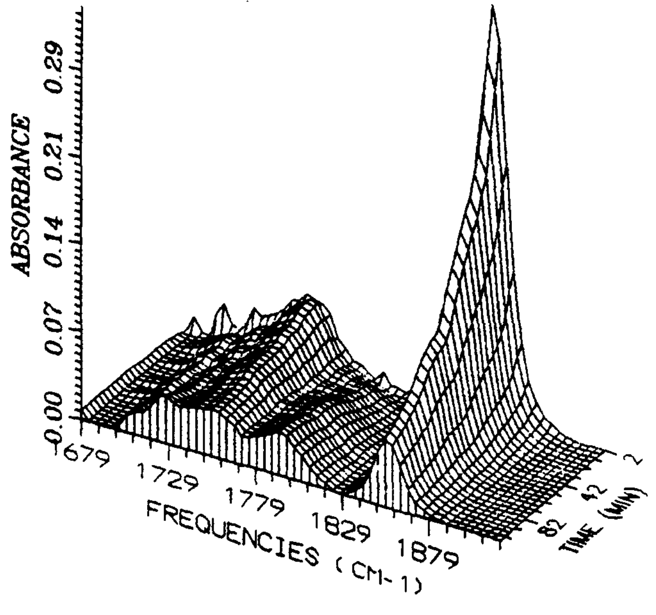


FIGURE 3 SS for *ν*(C=O) and *ν*(NO) vibrations.

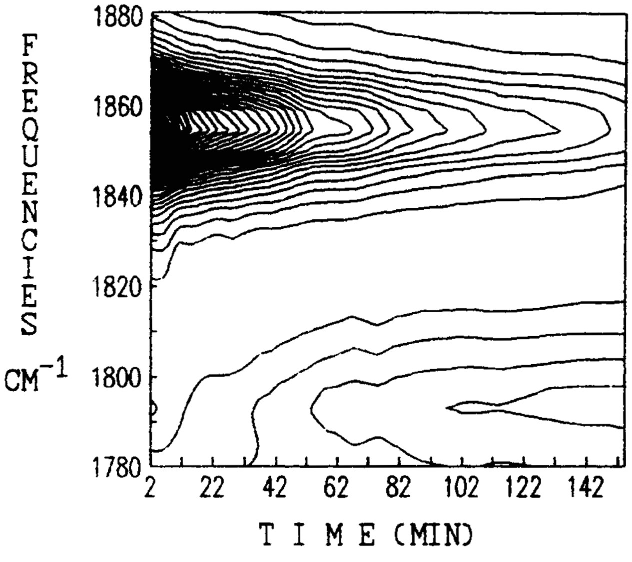


FIGURE 4 SM in the 1880–1780 cm^{-1} interval during the first ~152 minutes of the reaction.

product (3) first appears and then grows. At the same time, in this spectral range, the appearance of a new absorption band at 1752 cm^{-1} due to the vibration ν(CO) is noted. The intensity of this band steadily decreases until it disappears completely after about 40 minutes. The appearance of this new vibration ν(CO) can be explained by the fact that, during the reaction, a new intermediate is formed. It is known [6] that, for cation (1), the addition reaction of a suitable nucleophile to the carbon atom of the CO ligand is most specific. Taking into account the ambident nature of the P–S bond in the thioester of the given P(III) acid [7], it is possible to assume that the same type of reaction is attributable to the formation of either of the intermediates (4) or (5) in the reaction of 1 with 2.

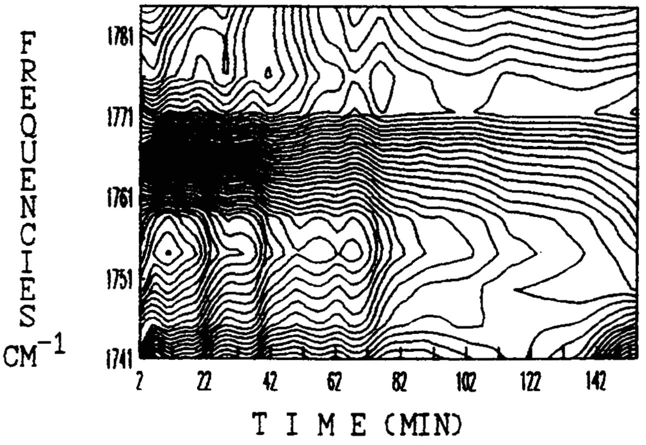


FIGURE 5 SM in the 1780–1740 cm^{-1} interval during the first ~152 minutes of the reaction.

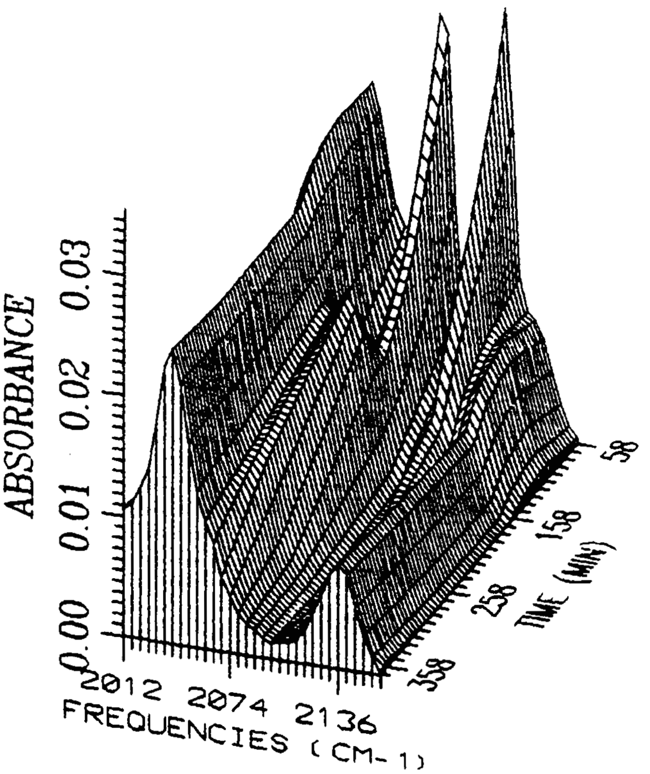
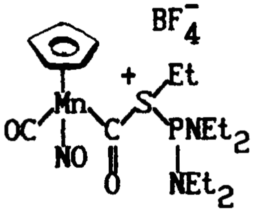


FIGURE 6 SS in the region of the CO vibrations for a hermetically sealed sample cell.



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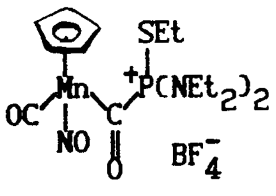

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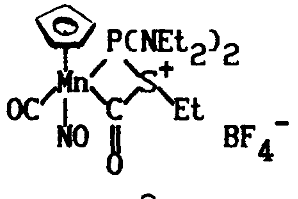
Perhaps both 4 and 5 are formed at the earlier stages of the reaction. It also seems reasonable to assume that compound (4) would be preferable as an intermediate product. Besides, when analyzing the SM (Figure 5), it is seen that, while the ~1752 cm^{-1} band decreases, the intensity of the absorption near 1776 cm^{-1} increases (Figure 5). This absorption band is related to the vibration of the C=O group of another intermediate (6) having a cyclic system, where the frequency of the ν(CO) is higher than that of compound (4) [8].



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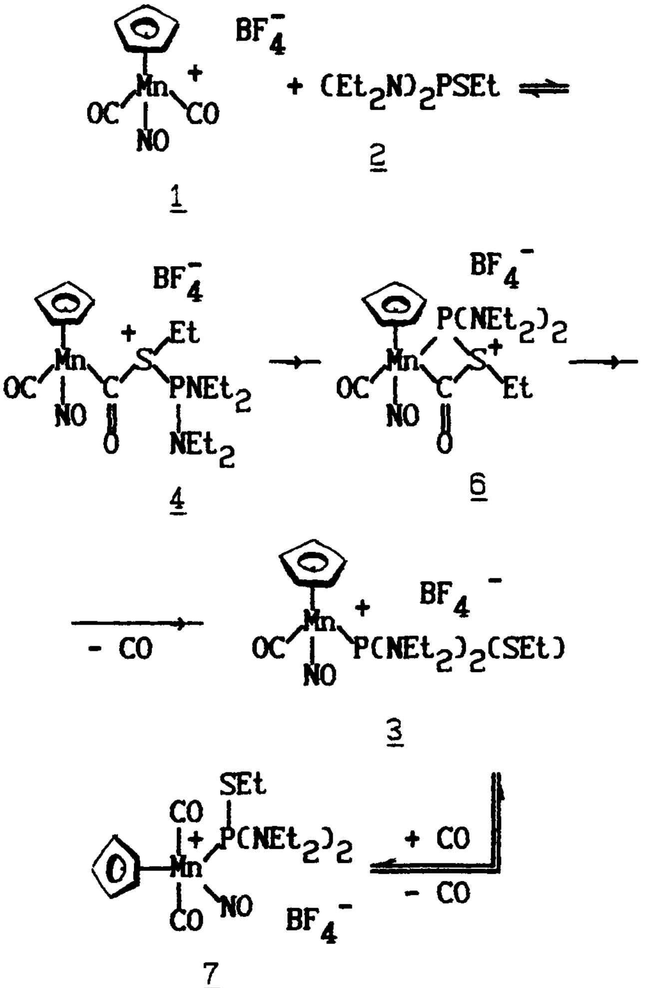
Later, the alteration of the ~1776 cm^{-1} band is masked by the beginning of growth of the ~1799 cm^{-1} band related to the stretching mode ν(CO) of the final product (**3**).

On the basis of our results, and taking into account pertinent literature data [7], we assume that the reaction of the cation (**1**) with the diamidothiophosphite (**2**) proceeds as follows.



The nucleophilic attack on the carbon of a CO ligand of (**1**) takes place in the first stage of the reaction, leading to the transition compound (**4**). The latter is in equilibrium with its precursors. Obviously, the equilibrium can be shifted to the unstable cyclic complex (**6**) due to the donation of the phosphorus lone pair to the Mn atom. Compound (**3**) is formed via rupture of the weak Mn–C and C–S bonds with concomitant formation of CO. The process is followed spectroscopically by the appearance of carbon monoxide.

For the process to be more obvious, we repeated the reaction under consideration in a hermetically sealed sample cell where the exit of gaseous CO from the reaction zone is small. Indeed, the IR spectra (Figure 6) recorded under such conditions showed the ~2136 cm^{-1} band, which belongs to the CO-stretching vibration of the carbon monoxide [8]. During the course of the reaction, the absorption band near 2060 cm^{-1} (Figure 2) was detected. This spectral phenomenon is more clearly apparent when the spectra of the products contained in a hermetically sealed sample cell are recorded (Figure 6). [The position of this absorption band is close to the vibration ν(CO) in the initial reagent (**1**)]. The intensity of the ~2136 cm^{-1} band subsequently decreases, but the band does not disappear. Perhaps one can concede that a new compound (**7**) has been formed. The symmetric and nonsymmetric vibration ν(CO) near 2060 cm^{-1}, as in the spectra of the compound (**1**), are degenerate owing to the fact that both CO groups in complex (**7**) occupy apical positions. When the intensity of the ~2060 cm^{-1} band increases (which involves growth in the concentration of **7**), there occurs a simultaneous decrease in the intensity of the 2136 cm^{-1} band (pertaining to carbon monoxide) and the growth of the intensity of the ~2039 cm^{-1} band for (**3**) is slowed down (Figure 6). Taking such dynamics into account, we assume that compound (**7**) is not involved in the formation of compound (**3**) but is the result of a reaction between carbon monoxide and the product (**3**). On removal of CO from the reaction mixture, the occurrence of this process is observed only to a considerably lesser extent.

CONCLUSIONS

Our FT-IR investigation of the reaction of *S*-ethyl-*N,N*-tetraethyldiamidothiophosphite with [η-Cp-Mn(CO)$_2$(NO)]$^+$BF$_4^-$ has made it possible for us to examine the SS and SM approaches. We believe that we have confirmed the formation of a few intermediates, and we are able to suggest a conceivable path for the reaction.

EXPERIMENTAL

The IR spectra were recorded by an FTIR spectrometer IFS-113V (Bruker) in the region of 400–4000 cm^{-1}. The investigation of the reaction was performed in a sample chamber of the spectrometer. We used sample cells with KRS-5 windows. Reagents (**1**) and (**2**) were mixed in acetonitrile solution and immediately placed in a sample cell. The spectra were then recorded during 3 hours at intervals of 3 minutes.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation of Fundamental Research (Grant No. 93-03-5830).

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