

THE USE OF POLYMERS AS MATRICES FOR ORGANOMETALLIC PHOTOCHEMICAL REACTIONS *

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Summary

A matrix technique for the study of photochemical preparation of unstable and air-sensitive organometallic compounds is described. The matrix used is a film of inert polymer, such as polytetrafluorethylene (PTFE). The films containing the compounds can be handled under normal ambient conditions. The method is used to study the products and photochemical reactions of pentacarbonyliron with olefins.

Introduction

It has long been known that pentacarbonyliron reacts photochemically with dienes to produce dienetricarbonyliron compounds [1]. More recently, bis-(diene)monocarbonyliron compounds has been reported [2]. In the case of low molecular weight dienes these products are rather air-sensitive and difficult to handle. The reaction of eneacarbonyldiiron with ethylene produces a very unstable and air-sensitive compound, ethylenetetracarbonyliron [3]. This compound was, however, successfully isolated in an argon matrix [4].

The matrix isolation method has been extensively used to study monomolecular photochemical processes of transition metal carbonyls and related species [5], although, there is no report, to date, on the study of bimolecular processes in matrices. However, low temperature matrices such as inert gases, methane or N₂ require the use of very expensive low temperature equipment and high vacuum systems.

The study of carbonyl complexes is facilitated by their high intensity infrared absorptions in the $\nu(\text{C}=\text{O})$ frequencies, and for a matrix to be useful it must be transparent in the region needed for spectral examination. Most polymers

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are transparent in the frequency region between 2200 and 1600 cm^{-1} . The use of polymers at ambient temperature also permits a higher mobility of molecules within the bulk, reducing the need for high reagent concentrations which would be required to study bimolecular processes when using frozen gases.

Radiation polymer chemists have for a long time used high energy radiation rather than light, arguing that light does not penetrate polymers enough to produce any significant bulk modification [6]. However, in a previous paper [7] we reported on the formation of a composite by the UV irradiation of PTFE pretreated with vinyl acetate. One of us reported [8] that pentacarbonyliron sorbed in PTFE undergoes a photochemical reaction on exposure to sunlight, producing eneacarbonyldiiron.

In this paper we report studies of the photochemical reactions of pentacarbonyliron with olefins in a PTFE room-temperature matrix. The reaction with the dienes butadiene and isoprene in the matrix produced not only dienetricarbonyliron but also bis(diene)monocarbonyliron compounds. With ethylene we observed the formation of ethylenetetracarbonyliron and with acetylene we observed changes in the infrared spectrum which can be assigned to the formation of acetylenetetracarbonyliron.

In all cases the films were handled under normal ambient conditions. In the case of films containing the dienetricarbonyliron compounds, heating to 160°C did not produce changes in the infrared spectra.

Experimental

PTFE samples were 0.2 mm thick sheets fabricated from DuPont Teflon by Incoflon. Butadiene and isoprene were used as furnished by Petroquimica União and EGA Chemie. Ethylene and acetylene were furnished by White-Martins. Pentacarbonyliron was donated by BASF do Brasil.

The light source used was an adapted Philips HPL-N 125 W lamp [9] in a water-cooled pyrex jacket.

In a typical experiment we soaked the polymer film in a solution of pentacarbonyliron in hexane for 24 hours, washed it with ethanol and measured its infrared spectrum. In the reaction with isoprene, we then soaked the same film in pure isoprene for 24 hours and again measured its infrared spectrum. In the case of butadiene, the pentacarbonyliron-containing film was placed for 24 hours in the photolysis apparatus filled with gaseous butadiene under normal pressure. The films pretreated as above were irradiated using a pyrex filter and the reaction was followed by measuring the infrared spectra of the films. The radiation time necessary to obtain complete reaction ranged from 30 to 120 minutes.

Only during the treatment of the films with the pentacarbonyliron solution is an argon atmosphere necessary. After this, the films can be handled under normal ambient conditions.

The reactions were followed using a Perkin-Elmer model 337 Infrared spectrophotometer. Determination of the position of the peaks were made in a Perkin-Elmer 399 B Infrared Spectrophotometer. All spectra were measured using a film with similar thickness in the reference beam of the spectrophotometer.

Results and discussion

In Figure 1 we show a typical sequence of spectra. Spectrum 1a shows the sorption of pentacarbonyliron by PTFE, spectrum 1b shows the same film after treatment with butadiene. In spectrum 1c and 1d we show the photolysis products, butadienetricarbonyliron and bis(butadiene)monocarbonyliron. The compounds obtained in the PTFE matrix are stable to long exposure to air or even to pumping air through the film. The infrared spectra of the films containing butadienetricarbonyliron and isoprenetricarbonyliron did not show any change after they had been heated to 160°C.

In Table 1 we present the observed frequencies in the $\nu(\text{C}=\text{O})$ region after the photolysis of the treated films. Comparison of the data with the literature confirms the formation of dienetricarbonyliron [10], bis(diene)monocarbonyliron [2] and ethylenetetracarboxyliron [3,4] compounds. The small shift in

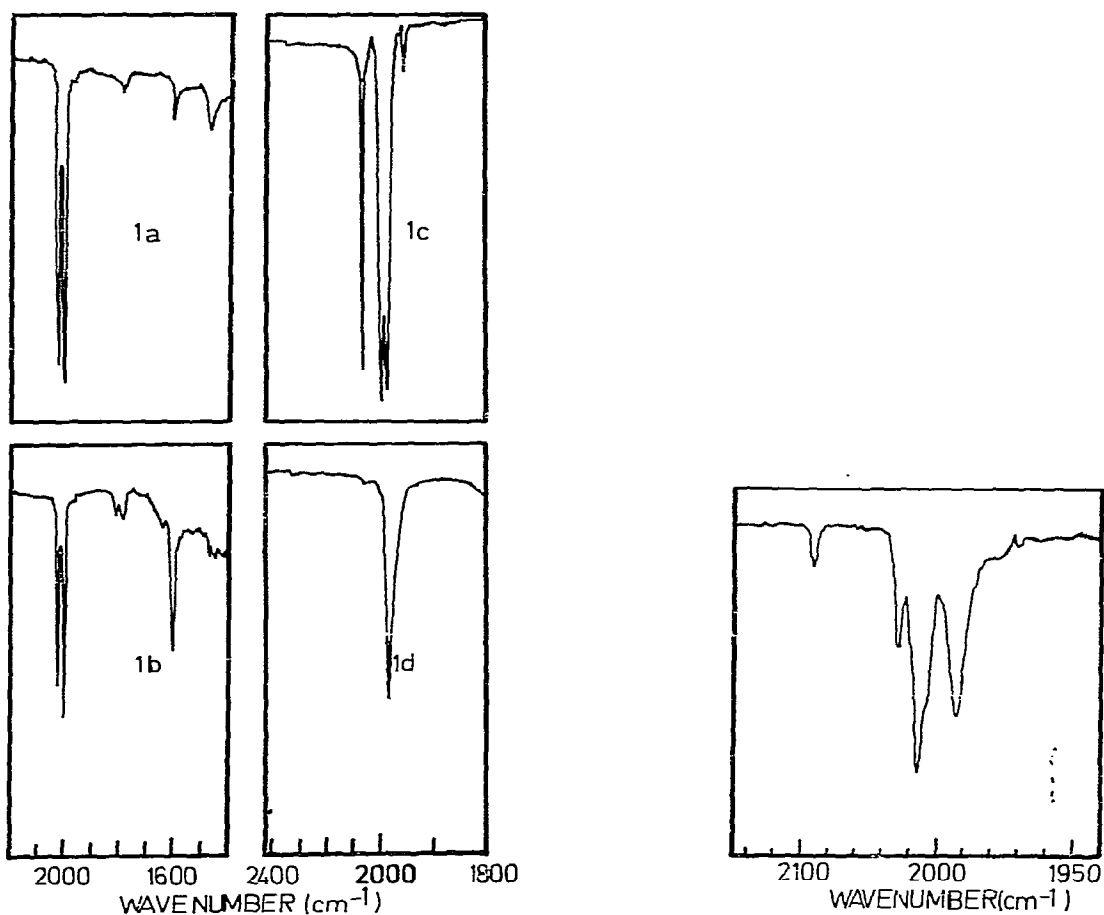


Fig. 1. Infrared spectra of the treated and the irradiated films, in the region of the $\nu(\text{C}=\text{O})$ frequencies. 1a, $\text{Fe}(\text{CO})_5$; 1b, $\text{Fe}(\text{CO})_5$ and C_4H_6 ; 1c, one hour of photolysis; 1d, two hours of photolysis.

Fig. 2. Infrared spectra of the ethylenetetracarboxyliron compound in the PTFE matrix.

TABLE 1

OBSERVED INFRARED FREQUENCIES IN THE $\nu(\text{C}=\text{O})$ REGION OF THE TREATED PTFE FILMS, AFTER PHOTOLYSIS

Treatment	$\nu(\text{C}=\text{O})$ (cm^{-1} , ± 2)	Product
$\text{Fe}(\text{CO})_5$	2024s, 2005s ^a	—
$\text{Fe}(\text{CO})_5, \text{C}_4\text{H}_6$	2060s, 1995s, 1984s	$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_6)$
$\text{Fe}(\text{CO})_5, \text{C}_4\text{H}_6$	1985s ^b	$\text{Fe}(\text{CO})(\text{C}_4\text{H}_6)_2$
$\text{Fe}(\text{CO})_5, \text{C}_5\text{H}_8$	2055s, 1991s, 1980s	$\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_8)$
$\text{Fe}(\text{CO})_5, \text{C}_5\text{H}_8$	1985s ^b	$\text{Fe}(\text{CO})(\text{C}_5\text{H}_8)_2$
$\text{Fe}(\text{CO})_5, \text{C}_2\text{H}_4$	2088s, 2024m, 2008s, 1989s	$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$
$\text{Fe}(\text{CO})_5, \text{C}_2\text{H}_2$	2095w, 2025s, 2004s, 1990sh, 1967w	$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_2)$

s, strong; m, medium; w, weak; sh, shoulder. ^a Before photolysis, ^b Longer photolysis time.

the position of the peaks, in comparison with the literature data, is due to the difference in the sample environments. Our measured peak positions may be more comparable with pure samples, but data on these are not available.

In case of ethylene, we did not pretreat the PTFE film containing pentacarbonyliron with the olefin, but instead we irradiated the film in the presence of gaseous ethylene. The product compound was previously reported by Murdoch and Weiss [3], who reported three peaks in the $\nu(\text{C}=\text{O})$ region of the infrared spectrum (2088, 2007 and 1986 cm^{-1}) and a shoulder at 2013 cm^{-1} . Newlands and Olgvie [4], working in an argon matrix, observed only three bands in the $\nu(\text{C}=\text{O})$ region (2090, 2009 and 1992 cm^{-1}), which would suggest a C_{3v} point group symmetry for this compound. Since this symmetry seems very improbable for such a compound, we believe that the fourth band, observed by us at 2024 cm^{-1} (Fig. 2 and Table 1), is sufficient evidence to assign a C_{2v} point group symmetry for this compound. This suggests the coordination of the ethylene molecule at the equatorial position of a trigonal bipyramid.

In the reaction of acetylene with pentacarbonyliron we have evidence for the formation of a product, probably acetylenetetra carbonyliron. The modifications that we observe in the spectrum cannot be assigned to an iron carbonyl fragment. However, even after 24 hours of photolysis the reaction was incomplete and the strong absorptions of pentacarbonyliron precluded a better interpretation of the results.

The stability of compounds such as ethylenetetra carbonyliron to air when obtained in the polymer matrix provides evidence that the compounds are not being formed on the surface of the polymer but in its bulk. In a previous paper [7] we reported the formation of poly(vinyl acetate) in the bulk of PTFE, producing a composite material. Another similar bulk product formation was observed when Fe_2O_3 was formed from pentacarbonyliron sorbed in PTFE [11]. Also, reduction of the thickness of the film to 70% by sanding both surfaces does not produce any major change in the infrared spectra.

It is very probable, although not measured that, after sorption, the molecules of the reagents are lodged on the amorphous sites of the polymers. This corroborates with the observation that sorption of pentacarbonyliron increases as the degree of crystallinity of polytetrafluorethylene decreases [11]. In these sites the sorbed compounds are protected against oxidation by air but have suf-

ficient mobility to react. The substitution of four carbonyls by two diene units also provides evidence that the local concentration of reagents is sufficiently high. The same reaction in solution requires a tenfold excess of the ligand and 48 hours of photolysis [2].

Besides the fact that fluorocarbon polymer chains, such as PTFE, do not absorb light above 200 nm, the occurrence of these photochemical processes in the bulk of the polymer films is evidence that there is a reasonable amount of light penetration in the films. Also, the relatively short photolysis time (30–120 min) required in the reactions, compared to solution experiments, corroborates these conclusions.

In the case of low-temperature matrices the sorts of reactions that may occur photochemically are very limited by the restrictions of the so-called "cage effect" [5]. It is generally difficult to produce a species by an in situ photolysis in low-temperature matrices by photoejection of a ligand because the molecule is usually too large to squeeze readily through lattice interstices and away from the newly formed unstable species. Thus, in the low-temperature matrices, the two fragments held together in the matrix cage recombine to reform the parent molecule [5]. In the case of our room temperature polymer matrices the molecules held in the amorphous sites apparently have a much higher mobility, in such a way that the carbon monoxide ligand squeezes away and the other ligand approaches the coordinatively unsaturated species formed. Alternatively, the concentration of the reagent molecules in the amorphous sites is so high that mobility may not be necessary to obtain a ligand exchange, thus making possible a bimolecular reaction in the matrix. Again, this is an advantage of the polymer matrix technique in comparison to the low-temperature matrices where the local concentrations of light-sensitive molecules are normally very low.

We believe that our method provides a valuable technique for the study of the infrared spectra of species formed by IR radiation processes since it uses a highly inert matrix in a very convenient way. We are currently extending these studies to other polymer matrices, such as polyethylene.

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References

- 1 R. Pettit and G.F. Emerson, *Adv. Organometal. Chem.*, **1** (1964) 1.
- 2 E. Koerner von Gustorf, J. Buchkremer, Z. Pfeiffer and F.-W. Grevels, *Angew. Chem.*, **83** (1971) 249.
- 3 H.D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **46** (1963) 1588.
- 4 M.J. Newlands and J.F. Olgvie, *Can. J. Chem.*, **49** (1971) 343.
- 5 J.K. Burdett, *Coord. Chem. Rev.*, **27** (1978) 1.
- 6 N.A.J. Platzer in R.F. Gould (Ed.), *Irradiation of Polymers*, Amer. Chem. Soc. Publications, Washington, 1967, pp. vii.

- 7 M.A. De Paoli, I.T. Tamashiro and F. Galembeck, *J. Polym. Sci., Polym. Lett. Ed.*, **17** (1979) 391.
- 8 F. Galembeck, S.E. Galembeck, H. Vargas, C.A. Ribeiro, L.C. Miranda and C. Glizzon, in K.L. Mittal (Ed.), *Surface Contamination*, Plenum Press, New York, 1979, pp. 54-71.
- 9 M.A. De Paoli and C.F. Rodrigues, *Quimica Nova*, **1** (1978) 16.
- 10 M.A. Busch and R.J. Clark, *Inorg. Chem.*, **14** (1975) 219.
- 11 F. Galembeck, *J. Polym. Sci., Polym. Lett. Ed.*, **16** (1978) 3015.