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Polymers as Matrices for Photochemical Reactions of Organometallic Compounds

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ABSTRACT

A new matrix technique developed in our laboratory for the study of bimolecular photochemical processes and the isolation of unstable and air-sensitive organometallic compounds is described. This technique provides a simple and unexpensive method for studying these compounds at room temperature and ambient atmosphere. The matrices used are films of inert polymers, such as polytetrafluorethylene (PTFE) and polyethylene (PE). We have used this method to study, by means of infrared (i.r.) spectroscopy, the photochemical products and reactions of ironpentacarbonyl with olefins, such as: ethylene, acrylic acid, methylacrylate, norbornadiene, butadiene and isoprene; as well as to study the photofragmentation of ironpentacarbonyl. Evidence indicates that, in addition to permitting work with these compounds at ambient conditions, the method has other advantages over the usual low temperature frozen gas matrices.

INTRODUCTION

The first attempt to use polymers as matrices for photochemical reactions was made by Massey and Orgel, by dissolving $M(CO)_6$ (M = Cr, Mo or W) in a solution of polymethylmetacrylate and evaporating the solvent, in such a way that the polymer was trapped in the matrix (1). Upon irradiation with u.v. light the polymer assumed the color of the $M(CO)_5$ fragment. After a period in the dark $M(CO)_6$ was regenerated. The same process was used to study the flash-photolysis of $W(CO)_6$ in a polystyrene matrix (2). The use of plastic films in photochemical experiments was also reported by Kellogg and Bennett (3) to obtain low optical density samples in such a way that the adsorbed acceptor did not absorb the residual donor phosphorescence. Other attempts to study photochemical processes in solid matrices at room temperature were made by Pitts and co-workers (4) working with alkaline-halide pellets, in this case the effect of the matrix in the photochemical process was the same as would be achieved by changing the solvent.

The matrix isolation method using frozen gases has been extensively used to study photochemical processes of transition metal carbonyls and related species (5), although there is no report, to date, on the study of bimolecular processes in these matrices, except for those cases where the second reagent is the matrix itself (6). Unfortunately, low-temperature matrices such as inert gases, methane or N_2 require the use of expensive low temperature/high vacuum equipment. Thus a better matrix isolation method is needed.

The sorption of ironpentacarbonyl by polytetrafluorethylene (PTFE) was reported, and it was shown that the degree of sorption depends inversely on the degree of cristallinity of the polymer (7). It was also reported that this compound undergoes, when sorbed, the same thermal reactions as in solution, without reacting with the polymer backbone (8). Later on, it was observed that sorption in PTFE of a photopolymerizable monomer, followed by u.v. irradiation, produces composite materials, such as polyvinylacetate in PTFE (PTFE-PVA) (9). Also the exposure to sun light of a PTFE film treated with $Fe(CO)_5$ was shown to produce the dimer $Fe_2(CO)_9$ (10).

The photochemical reaction of ironpentacarbonyl with dienes has long been known to produce dieneirontricarbonyl compounds (11). Also bis(diene)ironmonocarbonyl compounds are obtained by means of irradiation of $Fe(CO)_5$ in the presence of an excess of diene (12). The dieneirontricarbonyl compounds prepared with low molecular weight dienes are rather air-sensitive and difficult to handle. Known monoolefintetracarbonyliron(0) compounds are also unstable, unless electron-withdrawing groups are attached to the olefinic function. The reaction of eneacarbonyldiiron with ethylene produces a very unstable and air-sensitive compound, ethyleneirontetracarbonyl (13), which has also been identified in an argon matrix (14). The reaction of ironpentacarbonyl with substituted monoolefins has also been studied in solution (15).

The study of carbonyl complexes is facilitated by their high intensity absorption in the ν_{CO} frequency region of the infrared spectra. Thus, for a matrix to be useful it must be transparent in the region needed for spectral examination. Most polymers do not absorb in the region of frequencies between 2200 and 1600 cm^{-1}. On the other hand, the polymer should not absorb the radiation used to induce the photochemical process, not only because it would hinder the reaction, but also because such absorption would lend to degrade the polymer. Saturated hydro- or fluorocarbon polymers fulfill these requirements and can also be selected to have different degrees of cristallinity. The use of polymers at room temperature also permits a higher mobility of the molecules within the bulk, reducing the need for the high reagent concentration which are required to study bimolecular reactions in frozen gases.

In this article we describe the use we have made of polymer matrices such as PTFE and PE to study photochemical substitution of carbon monoxide ligands of ironpentacarbonyl by olefinic ligands.

In PTFE matrices, we have observed the formation of diene-irontricarbonyl and bis(diene)ironmonocarbonyl compounds from the reaction of ironpentacarbonyl with butadiene and isoprene and the formation of ethyleneirontetracarbonyl from the reaction with gaseous ethylene (16). In PE matrices we have observed the formation of compounds of the type $Fe(CO)_4L$, where L is acrylic acid, methylacrylate (17) or norbornadiene (18). In these cases it is assumed that the primary step in the photosubstitution of CO is excitation of $Fe(CO)_5$ followed by the loss of a CO ligand. Following this, we studied the photofragmentation of $Fe(CO)_5$ in a PE matrix (17), confirming observations obtained using frozen gas matrices (19).

In all cases the polymer films containing the compounds were handled at room temperature and under the ambient atmosphere.

MATERIALS AND METHODS

The polymer films were used as furnished. The PTFE films were 0.2 mm thick, fabricated from DuPont Teflon by Incoflon. The PE films were 1.0 mm thick fabricated from Poliolefinas. Ironpentacarbonyl was used as furnished by BASF do Brasil.

The sorption of ironpentacarbonyl in the polymer is carried out by soaking the film in a 10% solution of it in degased hexane. When using PTFE, 24 hours are necessary to obtain the highest degree of sorption, although this level, cannot be detected by weighing and does not saturate the i.r. spectrum (fig. 1a). With PE, five minutes of soaking in the same solution are sufficient to saturate the i.r. spectrum (fig. 1b). After 24 hours of soaking a 1% increase in the weight of the film can be detected. Polymers from other sources will probably require different sorption times due to variations in the degree of cristallinity. The polymer film must be washed with ethanol immediately after removal from the soaking solution, to prevent oxidation of ironpentacarbonyl on the surface, forming a layer of ironoxide. Only during soaking is an inert gas atmosphere necessary. Once ironpentacarbonyl is trapped inside the matrix it will not oxidize during the time required for the experiment.

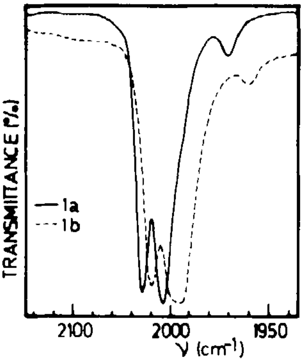

Fig. 1. I.r. spectra of the polymer films treated with ironpentacarbonyl, 1a) PTFE and 1b) PE.

Sorption of the second reagent, when used, depends on its physical state. For liquids, the film pretreated with $Fe(CO)_5$ is soaked in the second reagent for the time required to saturate it. For gases, the pretreated film is held in an immersion well irradiator filled with the gas under normal pressure. For solids, the pretreated film is soaked in a solution of the reagent and this solvent is subsequently evaporated from the film.

After this treatment the films are held in an immersion well apparatus and irradiated. A Philips HPK-125 W lamp was used for the experiments requiring vycor filters and an adapted (20) Philips HPLN- 125 W lamp was used when pyrex filters were required.

The reactions were followed using a Perkin-Elmer model 399 B double bean i.r. spectrophotometer using, for reference, a film with similar thickness. All spectra were measured with five times expansion in the abcissa. In our study of the photo-fragments of $Fe(CO)_5$ we irradiated the films directly in the i.r. spectrophotometer.

RESULTS AND DISCUSSION

Figure 2 shows a typical sequence of spectra for an experiment performed in PTFE. Fig. 2a is the spectrum of a film treated with ironpentacarbonyl and butadiene, Fig. 2b and 2c are the spectra of the same film after one hour of visible light irradiation and after two hours. These spectra correspond to those of butadieneirontricarbonyl (ν_{CO} = 2060, 1995 and 1984 cm^{-1}) and bis(butadiene)ironmonocarbonyl (ν_{CO} = 1985 cm^{-1}), respectively. A similar experiment using isoprene gave similar results (ν_{CO} = 2055, 1991 and 1980 cm^{-1}; ν_{CO} = 1985 cm^{-1}). The i.r. spectra of

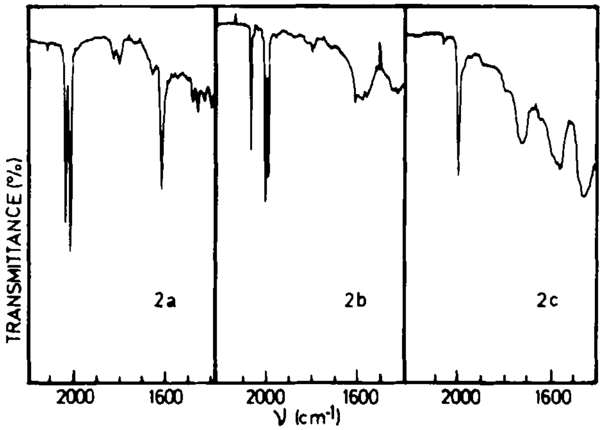

Fig. 2. I.r. spectra of a PTFE film: treated with $Fe(CO)_5$ and C_4H_6 (2a), irradiated during one hour (2b) and irradiated during two hours (2c).

these films do not change after one week of exposure to ambient conditions or even after pumping air through the films. Even heating the films containing the dieneirontricarbonyl compounds to 160°C produces no change in the spectra.

To use ethylene as the second reagent, the film pretreated with ironpentacarbonyl was placed in the immersion well irradiator, which was subsequently filled with ethylene under normal pressure. After 45 minutes of u.v. photolysis, all absorptions due to $Fe(CO)_5$ vanish and we observe four absorptions at: 2092, 2029, 2014 and 1993 cm^{-1} (fig. 3). These absorptions correspond to the substitution of one carbon monoxide by an ethylene. The substitution in the equatorial position of a trigonal bipyramid leads to a C_{2v} point group symmetry compound, which has four active absorptions in the ν_{CO} frequency region of the infrared spectrum. The product was previously reported by Murdoch and Weiss (13), who report three peaks in the ν_{CO} region (2088, 2007 and 1986 cm^{-1}) and a shoulder at 2013 cm^{-1}. Other authors working in an argon matrix observed only three bands (2090, 2009 and 1992 cm^{-1}) (14).

We also reacted acetylene with $Fe(CO)_5$ in the PTFE matrix, using the same conditions as with ethylene. The modifications observed in the spectrum can be assigned to a product, probably acetylene-irontetracarbonyl. However, even after 24 hours of photolysis the reaction is not complete and the strong absorp-

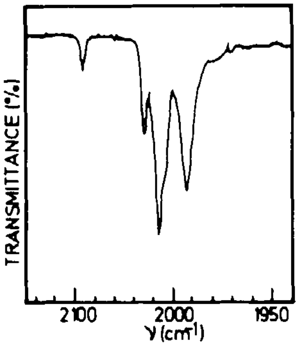

Fig. 3. I.r. spectrum of the ethyleneirontetracarbonyl compound in the PTFE matrix.

tions of ironpentacarbonyl preclude a better interpretation of the results.

As mentioned at the begining of this chapter, the degree of sorption of molecules by polymers depends inversely on the degree of cristallinity (8) and also on the square of the difference (δ polymer - δ sample), where δ is the Hildebrand's solubility parameter (21). In order to increase the concentration of reagents in the matrix we performed experiments with low-density PE which is highly amorphous, has a Tg bellow room temperature, and shows a high degree of sorption of liquids such as ironpentacarbonyl.

Irradiation of a PE film treated with $Fe(CO)_5$ and norbornadiene (NBD) produced interesting results. After three minutes of photolysis, four new bands are observed in the ν_{CO} frequency region of the i.r. spectrum (2098, 2032, 2020 and 2010 cm^{-1}) as well as a band at 1730 cm^{-1}. After further irradiation the 1730 cm^{-1} band becomes stronger and the other ν_{CO} bands vanish. The appearance of four ν_{CO} absorptions instead of three suggest the formation of the compound $(\eta^2\text{-NBD})Fe(CO)_4$ instead of the expected $(\eta^4\text{-NBD})Fe(CO)_3$ (23). A similar η^2-compound was reported (22) to be obtained by irradiating a solution of 5,6-dimethylene-7-oxabicylo|2,2,1|hept-2-ene and $Fe(CO)_5$. This product shows four ν_{CO} absorptions at 2097, 2032, 2017 and 1984 cm^{-1} (22). The band at 1730 cm^{-1} corresponds to a carbonyl inserted into a dimer of NBD (23). The formation of this dimer indicates that, in an intermediate step, two NBD entities must be bound as η^2-ligands to a single $Fe(CO)_3$, to subsequently dimerize and suffer carbonyl insertion (24). This intermediate has not been identified.

Formation of compounds of the type $Fe(CO)_4L$ can be also observed in a PE matrix. After one minute of photolysis of a PE film treated with ironpentacarbonyl and methylacrylate we observed the complete disappearance of the ν_{CO} bands of $Fe(CO)_5$ and the formation of four new bands at 2098, 2032, 2020 and 1996 cm^{-1} (fig. 4). These bands correspond to the compound methylacrylate-irontetracarbonyl. Further photolysis does not produce any significant change in the i.r. spectrum. In the case of acrylic acid, exposure of the treated film to u.v. light for long periods does not lead to the total consumption of $Fe(CO)_5$. In this reaction we observed, after irradiation, four new absorptions: 2098, 2034, 1978 and 1940 cm^{-1}.

In solution the photochemical substitution of carbon monoxide in $Fe(CO)_5$ is assumed to follows a S_N1 type mechanism (25). The excited molecule decays by loosing a ligand, producing a coordenatively unsaturated sixteen electron species, $Fe(CO)_4$, which is very reactive. Since this species is probably also formed in the polymer matrices, we performed an experiment in order to observe it. The i.r. spectrum in the region between 2200-1800 cm^{-1} of a film of PE saturated with ironpentacarbonyl was recorded immediately after three minutes of broad-band u.v. light irradiation. Two new absorptions are observed at 2063 and 1973 cm^{-1} and the band at 1998 cm^{-1} (mainly due to $Fe(CO)_5$) is more intense, in relation to the 2020 cm^{-1} band, than before photolysis. Irradiation with a Nernst glower decomposes the new species formed, while the residual $Fe(CO)_5$ absorptions persist. Kinetic measurements indicated that two different species are formed. One has an absorption at 1973 cm^{-1} and another covered

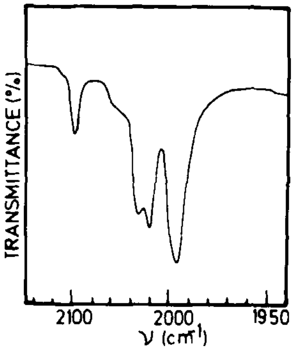

Fig. 4. I.r. spectrum of the mehylacrylateirontetracarbonyl compound in the PE matrix.

by the strong 1998 cm^{-1} band of ironpentacarbonyl. The other species absorbs at 2063 cm^{-1}. Kinetic measurements indicated a first order rate constant of 6.5 and 2.5 x 10^{-3} sec^{-1} for the disappearance of the bands at 2063 and 1973 cm^{-1}, respectively. The bands at 1973 and 1998 cm^{-1} are assigned to the photofragment $Fe(CO)_4$ and the other to a product of further fragmentation, probably $Fe(CO)_3$ (17).

Evidence that the compounds are reacting in the bulk of the polymer and not on the surface is given not only by the stability of the compounds observed, but also by the detection of unstable intermediates within the polymer matrix. The formation of composites (9) of PTFE also reinforces this conclusion. It is very probable, although not measured, that, after sorption, the molecules of the reagents are lodged in the amorphous sites of the polymers. This corroborates with the observation that sorption increases as the degree of cristallinity of the polymer matrix decreases. When lodged in the amorphous sites of the polymer, the molecules have a greater stability than when exposed to air, in the solid or in solution. This does not mean that they are "frozen" in the polymer cage since they have sufficient mobility to react. The substitution of four carbonyls of $Fe(CO)_5$ by two butadiene or isoprene molecules provides evidence that the local concentration of reagents is sufficiently high and that the carbon monoxide is lost at a sufficiently fast rate. The same reaction, in solution, requires 48 hours of irradiation with constant bubling of argon to remove CO (12). It is probable that the rate of diffusion of oxygen through the polymer is affected by this "amorphous sites insertion", on the other hand, the carbon monoxide desorption is sufficiently fast to preclude the regeneration of $Fe(CO)_5$ in the photofragmentation experiment (17, 26). Another argument favoring the fast desorption of CO is that, in several experiments, CO was not detected in the infrared spectra measured immediately after photolysis.

Radiation polymer chemists have, for a long time, neglected the use of light, using instead high energy radiation, based on the argument that light does not penetrate polymers well anough to produce significant bulk modification (27). In fact it is not possible to measure the u.v.-visible transmission spectra of thick polymer films (0.2-1.0 mm) by methods other than photoacustic spectroscopy (28). Although fluoro- or hydrocarbon chains, such as PTFE and PE, scatter considerably light above 200 nm, the occurrence of photochemical processes in the bulk of the polymer films is evidence that there is a reasonable amount of light penetration in the films. The relatively short photolysis time required for these reactions, compared to solution experiments, also corroborates this conclusion.

In the case of low-temperature matrices, the types of reactions that may occur are very limited by the so called "cage effect" (5). It is generally difficult to produce a species by an in situ photolysis in frozen gas matrices by photoejection of a ligand, because the molecule is usually too large to squeeze readily through the lattice intersticies and away from the newly formed unstable species. Thus, in the low temperature matrices, the two fragments are held together in the matrix cage, and recombine to give back the parent molecule. This effect is seen even in the case where the ligand is carbon monoxide, as is evidenced by the ease of recombination of carbon monoxide with $Fe(CO)_4$ in a frozen gas matrix (19). In the case of our room temperature polymer matrix, the molecules held in the amorphous sites of the polymer have, apparently, a much higher mobility. Due to this mobility, the second ligand can approach the unstable coordenatively unsaturated species formed by the photolysis, probably, at a non-diffusion controled rate.

These effects, higher mobility and high local concentration of reagents, make possible bimolecular reactions in the polymer matrices. These are among the advantages of this technique when compared to the low temperature matrices where the molecules are "frozen" in the lattice and the local concentration of light sensitive molecules is normally very low. We believe that our method provides a valuable technique for the study of the infrared spectra of species formed by radiation processes since it uses a highly inert matrix in a very convenient way.

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REFERENCES

(1) A.G. Massey and L.E. Orgel, Nature (1961), 1387.
(2) J.A. McIntyre, J. Phys. Chem., 74, 2403 (1970).
(3) R.E. Kellogg and R.G. Bennett, J. Chem. Phys., 41, 9042 (1964).
(4) J.N. Pitts Jr., L.D. Hess, E.J. Baum, E.A. Schuck and J.K.S. Wan, Photochem. Photobiol., 4, 305 (1965).
(5) J.K. Burdett, Coord. Chem. Rev., 27, 1 (1978).
(6) M. Poliakoff and J.J. Turner, J.C.S. Dalton, 1974, 2276.
(7) F. Galembeck, J. Polym. Sci., Polym. Chem. Ed., 16, 3015 (1978).
(8) F. Galembeck, J. Polym. Sci., Polym. Lett. Ed., 15, 107 (1977).
(9) M.A. De Paoli, I.T. Tamashiro and F. Galembeck, J. Polym. Sci., Polym. Lett. Ed., 17, 391 (1979).

(10) F. Galembeck, S.E. Galembeck, H. Vargas, L.A. Ribeiro, L.C.M. Miranda, and C.C. Glizoni, in "Surface Contamination", vol. 1, K.L. Mittal ed., Plenum Press, 1979, USA, pp 57-71.
(11) R. Pettit and G.F. Emerson, Adv. Organometall. Chem., 1, 1(1964).
(12) E. Koerner von Gustorf, J. Buchkremer, Z. Pfeiffer and F.-W. Grevels, Angew. Chem., 83, 249 (1971).
(13) H.D. Murdoch and E. Weiss, Helv. Chim. Acta, 46, 1588 (1963).
(14) M.J. Newlands and J.F. Olgivie, Can. J. Chem., 49, 343 (1971).
(15) W. Strohmeier, Angew. Chem., 76, 873 (1964).
(16) M.A. De Paoli, S.M. Oliveira and F. Galembeck, J. Organometall. Chem. in press.
(17) M.A. De Paoli and S.M. Oliveira, J.C.S., Chem. Comm. submited.
(18) M.A. De Paoli and S.M. Oliveira, unpublished results.
(19) M. Poliakoff and J.J. Turner, J.C.S. Dalton, 1973, 1351.
(20) M.A. De Paoli and C.F. Rodrigues, Quimica Nova, 1, 1, 16(1978).
(21) J.H. Hildebrand and R.L. Scott, "The Solubility of Non-Electrolytes", 3rd ed., Reinhold, New York, 1950.
(22) T. Boschi, P. Vogel and R. Roulet, J. Organometall. Chem., 133, C 36 (1977).
(23) C.W. Bird, R.C. Cookson and J. Hudec, Chem. Ind., 1960, 20.
(24) J. Mantzaris and E. Weissberger, J. Am. Chem. Soc., 96, 1880 (1974).
(25) E.A. Koerner von Gustorf, L.H.G. Leenders, I. Fischler and R. Perutz, Adv. Inorg. Chem. Radiochem., 19, 65 (1976).
(26) We are actually studying this from the point of view of "how much the presence of molecules in the amorphous sites of the polymer afects the gas diffusion through it".
(27) N.A.J. Platzer in "Irradiation of Polymers" R.F. Gould ed., Amer. Chem. Soc. Publications, 1967, USA, pp vii.
(28) F. Galembeck, C.A. Ribeiro, H. Vargas, L.C.M. Miranda and C.C. Glizoni, J. Appl. Polym. Sci., in press.