

THE PHOTOCHEMISTRY OF $\text{Cr}(\text{CO})_6$ IN HIGH PRESSURE LOW TEMPERATURE POLYMER MATRIX MONITORED BY FOURIER TRANSFORM INFRARED AND UV-VIS SPECTROSCOPY

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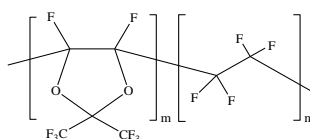
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Graphical abstract



Abstract

The aim of this work is to develop a new type of polymer matrix which can be used to study the reactive intermediates produced from UV photolysis of metal carbonyl complexes measured with FTIR as well as UV-vis spectroscopy. The photochemistry of $\text{Cr}(\text{CO})_6$ impregnated in Teflon-AF polymer with the presence of N_2 , CH_4 and even weak ligand i.e. Xe and He were conducted at extremely low temperature. Photolysis of $\text{Cr}(\text{CO})_6$ under N_2 environment produces up to four carbonyl groups being replaced with the N_2 . Meanwhile, the photochemistry of $\text{Cr}(\text{CO})_6$ under Xe and CH_4 produce the reactive complexes of $\text{Cr}(\text{CO})_5(\text{Xe})$ and $\text{Cr}(\text{CO})_5(\text{CH}_4)$ respectively. Teflon-AF was found to be the suitable matrix material as the $-\text{C}-\text{F}-$ bond binds very weakly to the metal center.

Keywords: Teflon-AF, matrix isolation, FTIR, UV-vis spectroscopy

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1.0 INTRODUCTION

This research focuses on studying the coordination of weak ligands to metal centres using the conventional matrix isolation technique i.e. the matrix isolation technique combined with polymer films. This technique has proved to be a very powerful tool for the characterization of reactive intermediates. However, one problem with current approach using polymer matrices is that the study of organometallic complexes is limited by the fact that the coordination of the alkane part of the polymer with unsaturated metal centres can prevent the coordination of other more weakly coordinating ligands to the metal. The formation of the metal-alkane bond is significant and can be stronger than the other ligands such as Xe, Kr or CO_2 .

Organometallic alkane complexes have been known for over 30 years. The first organometallic alkane complex was discovered by Poliakoff and Turner where they used matrix isolation to show that photolysis of $\text{Fe}(\text{CO})_5$ generates $\text{Fe}(\text{CO})_4$, which is sufficiently reactive to form complexes with CH_4 at 12 K[1]. The first

definitive study was reported by Perutz and Turner who found that photolysis of $\text{M}(\text{CO})_6$ generates $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}$ or W), which can react to form complexes with CH_4 at 12 K[2,3]. In addition, Perutz and Turner demonstrated that the position of the visible absorption band (λ_{max}) of $\text{Cr}(\text{CO})_5$ is very sensitive to the nature of the matrix.³ This was interpreted in terms of a specific interaction between the $\text{Cr}(\text{CO})_5$ fragment and the matrix material, a shift to shorter wavelength indicating a stronger interaction.

The first organometallic alkane complex characterized in solution was $\text{Cr}(\text{CO})_5(\text{cyclohexane})$; formed within 50 ns following UV flash photolysis of $\text{Cr}(\text{CO})_6$ in room temperature cyclohexane solution[4]. Since then organometallic alkane complexes formed in alkane solution have also been observed for $\text{CpM}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_{14})^5$ ($\text{M} = \text{V}, \text{Nb}$ or Ta), $\text{Cp}'\text{M}(\text{CO})_2(\text{L})$ [5,6,7]. ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_5$ (Re only); $\text{M} = \text{Mn}$ or Re ; $\text{L} = \text{CH}_4, n\text{-C}_2\text{H}_6, n\text{-C}_7\text{H}_{16}$ or $c\text{-C}_6\text{H}_{12}$ (Mn only)), $\text{Fe}(\text{CO})_4(\text{L})^8$ [$\text{L} = \text{ROH}, \text{SiEt}_3$ or C_5H_8] and $(\text{CO})_5\text{Cr}(\text{NC}_4\text{H}_8)\text{CH}_3$ ⁹.

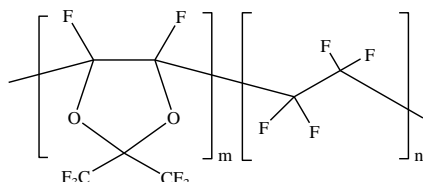
Apart from studies on organometallic alkane complexes, there is also considerable interest in

organometallic noble gas complexes. The organometallic noble gas complex was first characterized in the same year as its alkane analogue by Poliakoff and Turner using matrix isolation [1]. They demonstrated that $\text{Fe}(\text{CO})_5$, when photolysed in frozen Xe at 12 K, forms the complex $\text{Fe}(\text{CO})_4\text{Xe}$. Using a similar method, Perutz and Turner generated $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$; $\text{L} = \text{Xe}, \text{Kr}$ or Ar) from the photolysis of $\text{M}(\text{CO})_6$ in matrices at 20 K [3]. Other organometallic noble gas complexes characterized by matrix isolation include, *fac*-(η^2 -dfepe) $\text{Cr}(\text{CO})_3\text{Xe}$ (dfepe = $(\text{C}_2\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{F}_5)_2$) [1], $\text{Ru}(\text{CO})_2(\text{PMe}_3)_2\text{Xe}$ [1] and $(\text{dmpe})\text{Ru}(\text{CO})_2\text{Xe}$ (dmpe = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) [12].

Organometallic noble gas complexes have also been observed in solution. Simpson *et al.* [13] characterized $\text{Cr}(\text{CO})_5\text{Xe}$ at cryogenic temperatures in liquefied Xe (lXe) at -98°C and liquefied Kr (lKr) doped with Xe at -122°C using conventional FTIR spectroscopy following UV photolysis of $\text{Cr}(\text{CO})_6$. Since then, a range of organometallic noble gas compounds have been observed in various medium such as in the gas phase [14,15] and in supercritical fluids at room temperature [6,16, 17, 18-20]. It was shown by theoretical studies on $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$ and $\text{L} = \text{Ar}, \text{Kr}, \text{Xe}$), that the geometry of pentacarbonyl was not influenced by the binding of noble gases and there was an increasing trend in the bond energies for the metals $\text{Cr} < \text{Mo} < \text{W}$ and for the noble gases $\text{Ar} < \text{Kr} < \text{Xe}$ [21].

2.0 EXPERIMENTAL

$(\text{CO})_6$ was impregnated into Teflon-AF (Scheme 1) disc using supercritical CO_2 (sc CO_2) [16,22]. Supercritical CO_2 is relatively a good solvent for nonpolar organometallic and because the gas like nature; this property means that polymers can be impregnated without leaving any solvent residues [23]. A small amount of material together with a polymer disc were placed in a high pressure IR cell and pressurised with ca. 1800 psi of CO_2 at 41°C yielding low concentration (ca. 10^{-3} M) of metal carbonyl solution in sc CO_2 . The metal carbonyl complex that dissolved in sc CO_2 penetrates the polymer disc and when the cell is depressurised, the metal carbonyl complex remains trapped in the polymer while the CO_2 , which is gaseous at atmospheric pressure diffuses quickly out of the polymer. The IR spectrum of impregnated discs was measured in several different sample spots in order to make sure that the material is distributed uniformly within the polymer.



Scheme 1 Chemical structure of Teflon-AF

3.0 RESULTS AND DISCUSSION

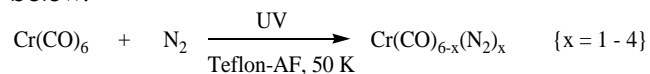
3.1 Photolysis of $\text{Cr}(\text{CO})_6$ in Dinitrogen at Low Temperature

Photolysis under N_2 provides a convenient test of how we can study the photochemistry reaction of hexacarbonyl complex in Teflon-AF at low temperature. The reaction has already been studied in liquid Xe and in a PE disc by Turner *et al.* [24] and Goff *et al.* [25] respectively. IR analysis of the products indicated that up to four of the six CO ligands could be substituted successively with N_2 groups in a PE disc. Meanwhile, irradiation of $\text{Cr}(\text{CO})_6$ and N_2 in liquid Xe solution leads to a greater degree of substitution *i.e.* up to five CO groups.

$\text{Cr}(\text{CO})_5(\text{N}_2)$ complex has also been postulated by Kelly *et al.* [26] at room temperature as an intermediate in the photochemical reactions of $\text{Cr}(\text{CO})_6$ in perfluoromethylcyclohexane solvent containing dinitrogen. The result of conventional flash photolysis experiment has shown an absorption at 353 nm which has been attributed to the transient $\text{Cr}(\text{CO})_5(\text{N}_2)$. $\text{Cr}(\text{CO})_5(\text{N}_2)$ was also characterised in solid nitrogen with absorption band at 364 nm [27].

In this work, the coordination of N_2 to the metal carbonyl impregnated in Teflon-AF has been characterized under 50 psi of N_2 at 50 K. An IR spectrum of $\text{Cr}(\text{CO})_6$ impregnated in Teflon-AF is shown in Figure 1(a) has single, $\nu(\text{CO})$ IR band of $\text{Cr}(\text{CO})_6$ (1991 cm^{-1} , FWHM = 5 cm^{-1}). Figure 1(b) shows the effect of UV photolysis following irradiation of the disc. It is clear that the parent band is bleached and a new photoproduct can easily be assigned to $\text{Cr}(\text{CO})_5(\text{N}_2)$ labelled as P by comparison with liquid Xe²⁴ and PE²⁵ data. The single $\nu(\text{NN})$ and three $\nu(\text{CO})$ bands are consistent with C_{4v} symmetry. The square-pyramidal geometry (symmetry C_{4v}) of the $\text{Cr}(\text{CO})_5$ framework has been characterised previously by a detailed analysis of the C-O stretching region of the IR spectra due to the isotopic variants $\text{Cr}(\text{CO})_5(\text{N}_2)$ and validated by a density theoretical study [28].

$\text{Cr}(\text{CO})_5(\text{N}_2)$ is itself photoreactive and upon further irradiation, bands that can be assigned to *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$ (labeled as S) and *fac*- $\text{Cr}(\text{CO})_3(\text{N}_2)_3$ (labeled as T) are produced. The *trans* (labeled as S') and *mer* (labeled as T') substituted isomers are also formed, but they can only be observed in the $\nu(\text{NN})$ region because their $\nu(\text{CO})$ bands are expected to be obscured by bands of other species. There is even evidence for the replacement of a fourth carbonyl group giving *trans*- $\text{Cr}(\text{CO})_2(\text{N}_2)_4$ (labeled as Q). An additional band at 2138 cm^{-1} is assigned to the uncoordinated CO molecule that is trapped within the Teflon-AF disc. The results are summarized in Scheme 2 below.



Scheme 2 Chemical equation between $\text{Cr}(\text{CO})_6$ and N_2

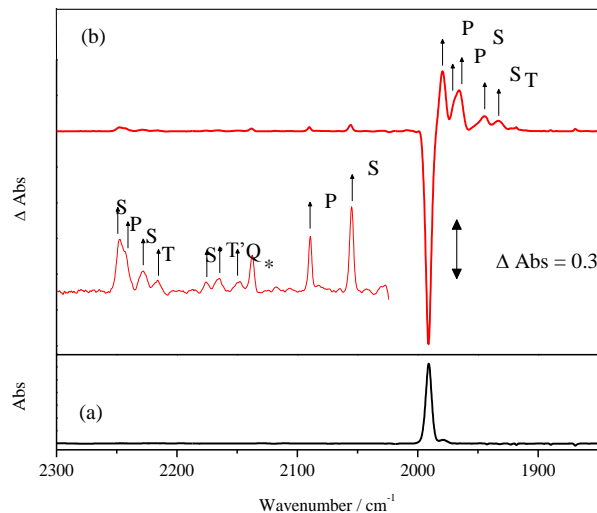


Figure 1 (a) FTIR spectrum of $\text{Cr}(\text{CO})_6$ in a Teflon-AF disc under N_2 at 50 K. (b) FTIR difference spectrum obtained following photolysis of the disc. The parent band decays with photolysis time with growth of bands assigned to $\text{Cr}(\text{CO})_5\text{N}_2$ (P), *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$ (S), *trans*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$ (S'), *fac*- $\text{Cr}(\text{CO})_3(\text{N}_2)_3$ (T), *mer*- $\text{Cr}(\text{CO})_3(\text{N}_2)_3$ (T') and *trans*- $\text{Cr}(\text{CO})_2(\text{N}_2)_4$ (Q). Asterisk is "free" CO. The difference spectrum was enlarged from (b) 2040 - 2300 cm^{-1}

The UV spectrum of Teflon-AF shows no significant absorbance in the near UV region, with the absorption maximum of Teflon-AF lying at ca. 205 nm. This means that UV photolysis of $\text{Cr}(\text{CO})_6$ using the medium pressure Hg arc lamp should have no effect on the polymer itself. Meanwhile, the UV spectrum of $\text{Cr}(\text{CO})_6$ impregnated in Teflon-AF shows two bands in the UV region (224 and 277 nm). UV irradiation of the impregnated disc at low temperature with the presence of N_2 shows a wavelength of maximum absorption at 356 nm,

Figure 2. If this value is compared with the photoproduct of $\text{Cr}(\text{CO})_6$ in C_7H_{14} solution saturated by N_2 (370 nm)²⁶ or low temperature N_2 matrix (364 nm)[27], it seems reasonable to assign this absorption to the $\text{Cr}(\text{CO})_5(\text{N}_2)$ species.

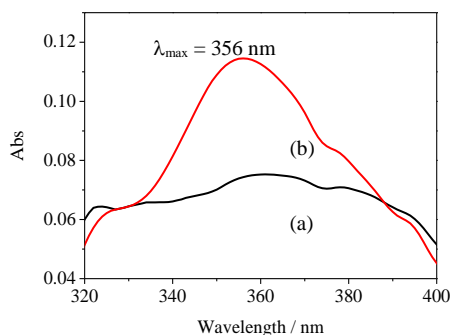


Figure 2 UV-vis spectra of (a) $\text{Cr}(\text{CO})_6$ in a Teflon-AF disc before photolysis at 50 K with N_2 and (b) after photolysis ($220 < \lambda < 600 \text{ nm}$)

3.2 Photolysis of $\text{Cr}(\text{CO})_6$ in Xenon at Low Temperature

Simpson *et al.* identified $\text{Cr}(\text{CO})_5(\text{Xe})$ using FTIR spectroscopy in liquefied Xe solution at a cryogenic temperature (-98 °C), providing the first evidence for the formation of rare gas complexes with significant lifetimes in solution.[13] Weiller was also able to detect $\text{Cr}(\text{CO})_5\text{Xe}$ in liquid Xe using rapid-scan FTIR[29]. Similarly, Sun *et al.* [30] have shown that rare gas complexes can be observed in fluid solution at room temperature following irradiation of metal carbonyls in supercritical noble gas solution at room temperature.

In this work, the reaction between $\text{Cr}(\text{CO})_6$ and Xe in a Teflon-AF disc at low temperature was characterized with regard to the ability of Teflon-AF to trap the low pressure gas at various temperature. The process starts with a low concentration of Xe (ca. 50 psi) pressurised in the system containing a Teflon-AF disc impregnated with $\text{Cr}(\text{CO})_6$ at room temperature. The system was then cooled to 100 K for the photolysis experiment. The parent spectrum has a single band at 1992 cm^{-1} , which decreases over the course of the experiment, whilst two intense bands at 1966 and 1939 cm^{-1} grow in over the course of the experiment. A closer look at the difference spectrum (Figure 3) reveals two weak bands in the higher wavenumber region that can be attributed to the uncoordinated CO band and a_1 symmetry band at 2137 and 2089 cm^{-1} respectively. By comparison with the room temperature photolysis of $\text{Cr}(\text{CO})_6$ in *scXe*, it is likely that $\text{Cr}(\text{CO})_5(\text{Xe})$ has formed in this reaction.[30] However, this photoproduct is assigned as $\text{Cr}(\text{CO})_5(\text{Y})$ (Y = unknown) for the time being, as based on the previous work in various matrix, all the single CO loss appear at similar wavenumbers, Table 1.

To gain an idea of the new complex that has formed in this experiment, the decay of photoproduct was monitored. At 100 K, this new complex was found to be stable however when warmed to 120 K, it started to decrease in intensity. On warming, some of the parent regenerated and new peaks at 2090, 2060, 2010 and 1951 cm^{-1} formed, Figure 4. The system was left at 120 K and at this temperature, the photoproduct peak at 1939 cm^{-1} was completely decayed but full regeneration of the parent peak was not seen. At the same time, the new peaks that formed on warming were seen to grow and these peaks may be assigned to the dinuclear species. A closer look at a much lower wavenumber of the spectrum, we were not able to observe any CO bridging band and the band positions also do not appear to match $\text{Cr}_2(\text{CO})_{10}$ [31,32]. The $\text{Cr}_2(\text{CO})_{10}$ species was only observed upon the reaction between $\text{Cr}(\text{CO})_4$ and the parent, $\text{Cr}(\text{CO})_6$ and thus this species is not expected to form as no evidence of loss of two carbonyl in our experiment.

The linear bridging CO group with no Cr-Cr bond, $(\text{OC})_5\text{Cr}(\text{CO})\text{Cr}(\text{CO})_5$ ³², i.e. $\text{Cr}(\text{CO})_6$ acting as a donor through a CO ligand forming a weak complex with $\text{Cr}(\text{CO})_5$ is a dinuclear species that could probably formed in this experiment. This dichromium species has never been isolated or even detected spectroscopically in low temperature matrix studies

including the reaction of Cr atoms with CO³³ or the photolysis of Cr(CO)₆. [2] However, Turner *et al.* [34] has postulated this dinuclear species based on colour changes and visible spectroscopy of the photolysis of Cr(CO)₆ in cyclohexane at room temperature. More recently, King *et al.* [32] have shown, via theoretical study, that (OC)₅Cr(CO)Cr(CO)₅ with C_{4v} symmetry possess a lower energy than previously studied CO bridging Cr-Cr bond Cr₂(CO)₁₁ structures [35]. Table lists the calculated and observed $\nu(\text{CO})$ frequencies for (OC)₅Cr(CO)Cr(CO)₅. The calculated values show a good match to my experimental values. Therefore, the dinuclear species formed in this experiment can be tentatively assigned as (OC)₅Cr(CO)Cr(CO)₅.

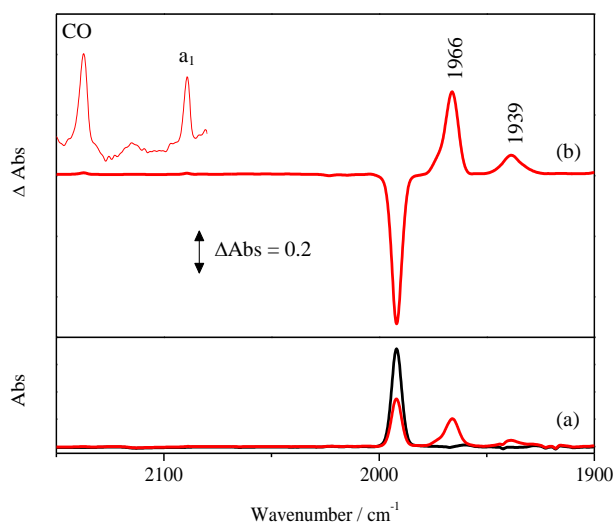


Figure 3 (a) FTIR spectra of Cr(CO)₆ in a Teflon-AF disc before and after UV photolysis at 100 K with added Xe. (b) FTIR difference spectrum of the same disc producing Cr(CO)₅(Y). Inset shows two small bands at higher wavenumber indicating "free" CO and $\nu(\text{CO})$ band of a₁ for the photoproduct

Table 1 Observed $\nu(\text{CO})$ cm⁻¹ stretching frequencies.

Complex	$\nu(\text{CO})$ cm ⁻¹	Ref.
Cr(CO) ₆	1981 (t _{1u})	80
	1982 (t _{1u})	13
	1992 (t _{1u})	This work
Cr(CO) ₅	1958 (e), 1949 (a ₁)	80
	1956 (e), 1926 (a ₁)	13
	1966 (e), 1939 (a ₁)	This work
(OC) ₅ Cr(CO)Cr(CO) ₅	2085 (a ₁), 2053 (a ₁), 2004 (a ₁), 1989 (e), 1956 (e), 1955 (a ₁), 1948 (a ₁)	80
	2090 (a ₁), 2060 (a ₁), 2010 (a ₁), 1994* (e), 1967* (e), 1966 (a ₁), 1951 (a ₁)	This work

*overlapping bands.

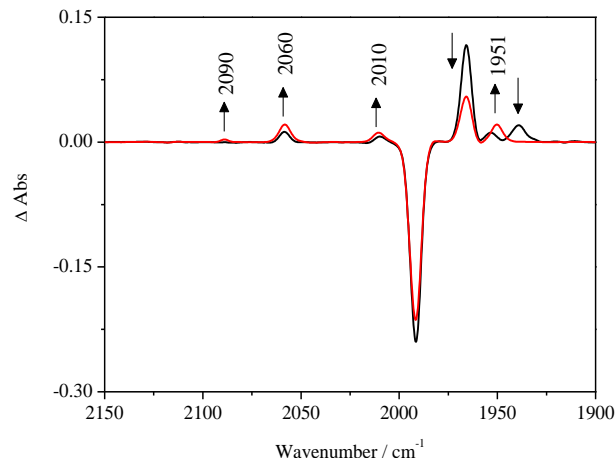


Figure 4 FTIR difference spectra at early (black) and later time (red) at 120 K showing the reducing of Cr(CO)₅(Y) bands and increasing of new bands at 2090, 2060 2010 and 1951 cm⁻¹

3.3 Photolysis of Cr(CO)₆ in CH₄ at Low Temperature

Photolysis of the disc at 100 K in the presence of CH₄ leads to a monodissociation of CO ligand giving a photoproduct with bands at similar positions as in experiment with added Xe. This Cr(CO)₅(Z) (Z = unknown) species however is reactive at 100 K and decays to partially reform the parent Cr(CO)₆ and dinuclear species with similar band positions as observed previously. The complete decay of the photoproduct band at 1940 cm⁻¹ gave a good fit to a bi-exponential function; where the fast component has a life time of ca. 20 min while the slow component has ca. 4 hours. The growth of the dinuclear species has a rate of ca. $7 \times 10^{-5} \text{ s}^{-1}$ which is almost identical to the value obtained for the decay of slow component. The fast component can be associated with the reformation of the parent (ca. $9.9 \times 10^{-4} \text{ s}^{-1}$). When the reactivity of Cr(CO)₅(Z) formed in CH₄ is compared with the reactivity of Cr(CO)₅(Y) formed in Xe (Section 3.2), it can clearly see that Cr(CO)₅(Z) is much more reactive than Cr(CO)₅(Y) which Cr(CO)₅(Y) only decays at temperature above 120 K while Cr(CO)₅(Z) decays at 100 K. Therefore, Cr(CO)₅(Z) can be tentatively assigned as a CH₄ complex and Cr(CO)₅(Y) as a Xe complex.

To aid this interpretation, the visible band of Cr(CO)₅(CH₄) was measured using UV-vis spectroscopy and found that λ_{max} lies at ca. 481 nm, which is lower than Cr(CO)₅(Xe) (ca. 486 nm). The blue shift is in agreement with those obtained in pure CH₄ and Xe matrices, 489 nm and 492 nm respectively [3]. Therefore, it is certain that Cr(CO)₅(Xe) and Cr(CO)₅(CH₄) complexes have formed within Teflon-AF disc at low temperature based on these two experiments.

3.4 Photolysis of $\text{Cr}(\text{CO})_5$ in Helium at Low Temperature

From evidence presented in the previous sections, Teflon-AF is a very promising matrix isolation polymer for studying the photochemistry reaction of metal carbonyl with no interference from the polymer even in a low concentration of reactant (e.g. Xe and CH_4). In this Section, the effect of adding more inert gas such as He, to the system was investigated. This is in order to examine whether the polymer can form a complex with the vacant site in $\text{Cr}(\text{CO})_5$ or if He can weakly interact with the metal centre.

In this section the photolysis experiment of $\text{Cr}(\text{CO})_5$ in Teflon-AF was carried out in the presence of He at 65 K. Figure 5 shows clear depletion of the parent ν_{CO} band (1993 cm^{-1}) with concomitant growth of new bands centred at 1971, 1967, 1946, 1938 and 1898 cm^{-1} . The assignment of these new peaks cannot be attributed to a single mononuclear CO loss intermediate since such a species cannot have more than two strong $\nu(\text{CO})$ bands. The production of five new bands may indicate that more than one primary photoproduct has been produced. These bands are not due to the dinuclear species as the $\nu(\text{CO})$ band positions do not match the literature values[32] and the values observed previously in our work (Section 3.2). Furthermore, all of the bands are not stable and decay at 65 K.

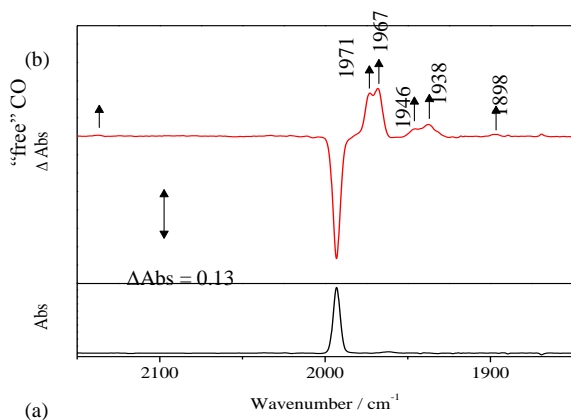


Figure 5 (a) FTIR spectrum of $\text{Cr}(\text{CO})_5$ in a Teflon-AF disc at 65 K before UV irradiation (b) FTIR difference spectrum obtained following UV photolysis

Based on a comparison with the work of Perutz and Turner [36] these peaks can be assigned to the formation of pentacarbonylchromium and tetracarbonylchromium complexes. It is however difficult to directly assign these bands to only two photoproducts because the pentacarbonyl species, $\text{Cr}(\text{CO})_5(\text{X})$ ($\text{X} = \text{unknown}$) should only have one very intense band (e symmetry) instead of the observed two (i.e. 1971 and 1967 cm^{-1}). Furthermore, as can be clearly seen in Figure 6, there are in fact more than two bands which appear as a shoulder at 1932 cm^{-1} and a band at 1942 cm^{-1} . These observations are consistent with not only two species being formed by the loss of

one and two carbonyl groups which we tentatively interpreted as the formation of $\text{Cr}(\text{CO})_5(\text{X})$ and $\text{Cr}(\text{CO})_4(\text{X})_2$, but another species is also formed producing $\text{Cr}(\text{CO})_5(\text{Y})$ ($\text{Y} = \text{unknown}$). Further work will be needed to clarify this point.

As mentioned previously, all peaks were observed to decay at 65 K and the bands were highly overlapped with each other; which makes the kinetics difficult to obtain. Generally, as these peaks decay, a small amount of dinuclear peaks with similar positions to those observed in previous sections were found to grow in with some regeneration of the parent peak. By relying on the peak positions, we can tentatively assign the two photoproducts as (a) polymer bound to the Cr metal centre forming $\text{Cr}(\text{CO})_5(-\text{C}-\text{F}-)$, with peaks at 1967 and 1938 cm^{-1} and (b) $\text{Cr}(\text{CO})_5(\text{He})$ with peaks at 1971 and 1942 cm^{-1} . The bands tentatively assigned to $\text{Cr}(\text{CO})_5(-\text{C}-\text{F}-)$ were shifted 4 cm^{-1} relative to $\text{Cr}(\text{CO})_5(\text{He})$. The assignments of these photoproducts are supported by the visible spectrum,

Figure 7. The visible bands for $\text{Cr}(\text{CO})_5(-\text{C}-\text{F}-)$ and $\text{Cr}(\text{CO})_5(\text{He})$ are ca. 552 nm and 513 nm respectively. Even though the shift is in agreement with those obtained from CF_4 and Ar matrices,[13] the separation between these values in this work is a lot bigger, Table 2.

The peaks at 1946 , 1932 and 1898 cm^{-1} can be tentatively assigned to the loss of two carbonyl groups from the metal centre producing a tetracarbonylchromium complex. Two possible products are $\text{Cr}(\text{CO})_4(-\text{C}-\text{F}-)_2$ and $\text{Cr}(\text{CO})_4(\text{He})_2$. We believe that the former is more favourable as the $-\text{C}-\text{F}-$ bond is more abundant in the system as compared with He. However, it should be considered that polymer binding gives more steric or bulky complex than He binding. The tetracarbonylchromium complex has a band in the visible which appears at ca. 409 nm (Figure 7) and this λ_{max} is similar to $\text{Cr}(\text{CO})_4$ formed in Ar environment[3]. Therefore, it is likely that the third photoproduct formed in this reaction is $\text{Cr}(\text{CO})_4$ with He coordinated weakly to the Cr metal centre but the fact that the position of $\text{Cr}(\text{CO})_4$ is not strongly dependent on the matrix[36] makes this assignment of this species is uncertain.

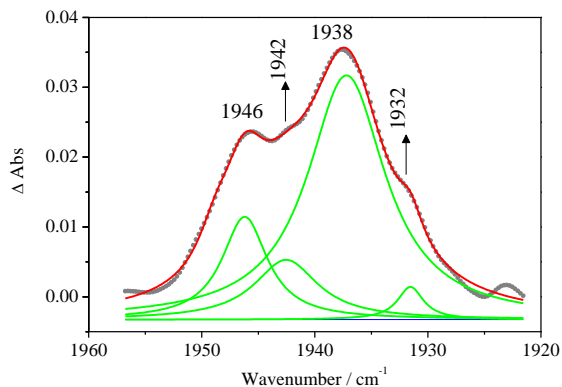


Figure 6 Peak fitting of bands from 1920 to 1955 cm^{-1} . The overlapped lines represent the individual components of the multi-lorentzian fit

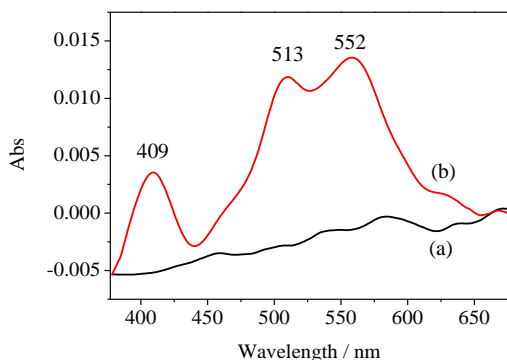


Figure 7 UV-vis spectra of $\text{Cr}(\text{CO})_5$ in a Teflon-AF disc at 65 K under He (a) before photolysis and (b) after photolysis ($220 < \lambda < 600 \text{ nm}$)

Table 2 Wavenumbers (cm^{-1}) and visible (nm) values of $\text{Cr}(\text{CO})_5$

$\text{Cr}(\text{CO})_5(\text{matrix})$	$\nu(\text{CO}) (\text{cm}^{-1})$			$\lambda_{\text{max}} (\text{nm})$
	ν_{tu}	ν_{e}	ν_{d}	
CF_4 , 20 K ^a	1994	1966	1935	547
Ar, 20 K ^a	1990	1965	1936	533
Xe, 20 K ^a	1982	1956	1926	492
CH_4 , 20 K ^a	1985	1960	1934	489
N_2 , 20K ^c	-	-	-	364
Teflon-AF, He, 65 K ^b	1993	1967 ^d , 1971 ^e	1938 ^d , 1942 ^e	552 ^d , 513 ^e
Teflon-AF, Xe, 100 K ^b	1992	1966	1939	486
Teflon-AF, CH_4 , 100 K ^b	1992	1967	1940	481
Teflon-AF, N_2 , 50 K ^b	1991	1979	1969	356

^aData from Ref³. ^bData from this work. ^cData from Ref²⁷. ^d $\text{Cr}(\text{CO})_5(-\text{CF}_3)$. ^e $\text{Cr}(\text{CO})_5(\text{He})$.

4.0 CONCLUSIONS

Teflon-AF was found to be a promising polymer for matrix isolation study particularly in monitoring the coordination of weak ligand. The polymer itself via $-\text{C}-$

$\text{F}-$ bond is reactive and competes with He to form complex with $\text{Cr}(\text{CO})_5$ at very low temperature. Although, this complex was found to be very unstable. However, the interaction of polymer bound species to the metal centre can be suppressed by addition of small amount of stronger ligand than He i.e. Xe and CH_4 . This means that Teflon-AF is a good alternative as a matrix material for studying the majority of photochemical reactions at low temperature.

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