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Substitution kinetics of $Cr(CO)_5(\eta^2$-Z-cyclooctene) with tetracyanoethylene

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Abstract

The weakly bound Z-cyclooctene (zco) ligand in $Cr(CO)_5(\eta^2$-zco) is replaced by tetracyanoethylene (tcne) at an observable rate in the temperature range between −5 and +10 °C yielding the complex $Cr(CO)_5(\eta^2$-tcne) as the final product. The kinetics of this substitution reaction was studied in toluene solution containing 5% by volume zco by quantitative FTIR spectroscopy. The substitution reaction obeys a pseudo-first order kinetics with respect to the concentration of the starting complex. The observed rate constant, k_{obs}, was determined at four different temperatures and five different concentrations of the entering ligand tcne in the range of 0.033–0.33 M. From the evaluation of kinetic data a possible reaction mechanism was proposed in which the rate-determining step is the cleavage of metal–olefin bond in the complex $Cr(CO)_5(\eta^2$-zco). A rate law was derived from the proposed reaction mechanism. From the dependence of k_{obs} on the entering ligand concentration, the rate constant k_1 for the rate determining step was estimated at all temperatures. The activation enthalpy ($\Delta H^{\circ} = 100 \pm 3$ kJ·mol^{-1}) and the activation entropy ($\Delta S^{\circ} = 59 \pm 3$ J·K^{-1}·mol^{-1}) were determined for this rate-determining step from the evaluation of k_1 values at different temperatures. The large positive value of the activation entropy is consistent with the dissociative nature of reaction. The large value of the activation enthalpy, close to the chromium–olefin bond dissociation energy, also supports this dissociative rate-determining step of the substitution reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chromium; Carbonyl; Cyclooctene; Tetracyanoethylene; Kinetics; Substitution; FTIR spectroscopy

1. Introduction

The photolysis of hexacarbonylmetal(0) in the presence of olefins such as ethene [1], Z-cyclooctene [2], E-cyclooctene [3], methylacrylate, dimethylfumarate [4], tetracyanoethylene [5] usually generates mono- and di-substitution products which can be isolated under different conditions and are relevant to photocatalytic processes [6] such as isomerization [7], hydrogenation [8], and hydrosilation [9] of mono- and diolefins. A recent kinetic study[10] on the photochemical conversion of $W(CO)_6$ into a *trans*-$W(CO)_4(\eta^2$-olefin$)_2$ complex using E-cyclooctene as a model olefin owing to its extraordinary co-ordination properties showed that the photolysis of $M(CO)_6$ in the presence of an olefin is expected to yield the stable final product *trans*-$M(CO)_4(\eta^2$-olefin$)_2$ through the intermediate $M(CO)_5(\eta^2$-olefin) and *cis*-$M(CO)_4(\eta^2$-olefin$)_2$ complexes. Indeed, with the exception of tetracyanoethylene (tcne) [5] and Z-cyclooctene (zco) for the case of chromium [2], *trans*-$M(CO)_4(\eta^2$-olefin$)_2$ is always found to be the final product of the photosubstitution of CO in the Group 6 metal carbonyls in the presence of excess olefin. Of the two exceptional cases, tcne forms the stable $Cr(CO)_5(\eta^2$-tcne) complex [5] as the electron withdrawing cyano groups lower the LUMO level of the olefin and increases its π-accepting ability, while *cis*-cyclooctene delivers the $Cr(CO)_5(\eta^2$-zco) complex (**1**) [2] as the sole product of the photosubstitution of $Cr(CO)_6$, probably because of the small size of chromium which can not accommodate more than one bulky olefin molecules. The latter product is metastable in and can be crystallized from the alkane solution doped with 5% b.v. Z-cyclooctene. The complex **1** is stable enough at room temperature in solid state, however, gradually decomposes with formation of $Cr(CO)_6$ in solution

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above −40 °C unless an excess of *cis*-cyclooctene is present [2]. Moreover, *Z*-cylooctene in **1** can be replaced by a variety of L-ligands present in the solution, such as carbon monoxide, alkylphosphine or olefines.

$$Cr(CO)_5(\eta^2 zco) + L \rightarrow Cr(CO)_5L + zco \qquad (1)$$

Therefore, the readily accessible complex **1** has been accepted as a useful source of $Cr(CO)_5$ unit. Although **1** has been used as $Cr(CO)_5$ transfer reagent in the preparation of many $Cr(CO)_5L$ complexes there exists no kinetic study on its relatively simple substitution reaction. Of particular interest is the substitution of *cis*-cyclooctene in **1** by another olefin as it would be one of the key reactions in the homogeneous catalysis [11]. Since *cis*-cyclooctene and tetracyanoethylene are the sole two olefins, which yield only $Cr(CO)_5(\eta^2\text{-olefin})$ complexes upon photolysis of the parent hexacarbonylchromium(0), the latter is the trivial olefin, which can be used for the substitution of the former. Here we report the kinetic investigation of the substitution of *cis*-cyclooctene in the very labile complex **1** by tetracyanoethylene (tcne) which forms $Cr(CO)_5(\eta^2\text{-tcne})$ (**2**), one of the most stable $Cr(CO)_5(\eta^2\text{-alkene})$ complexes. This is the first kinetic study of substitution reaction of a Group 6 monoolefin carbonyl complex. Since the π-accepting abilities of two olefins are quite different from each other their pentacarbonylchromium(0) complexes, **1** and **2**, exhibit CO stretching vibrations at different frequencies. Consequently, the IR absorption bands for CO stretching are readily distinguishable and can be used to monitor the substitution reaction.

2. Experimental

All of reactions and manipulations were carried out either in vacuum or under a dry and oxygen free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used. Hexacarbonylchromium(0), *cis*-cyclooctene, and tetracyanoethylene were purchased from Aldrich Chemical Co, Ltd., Dorset, UK. The thermal reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra at appropriate time intervals. NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.132 MHz for ^1H, and 100.613 MHz for ^{13}C). TMS was used as internal reference for ^1H- and ^{13}C-NMR chemical shifts. Infrared spectra were recorded from solutions on a Perkin–Elmer 16 PC FTIR spectrometer. Photochemical reactions were carried out in an immersion-well apparatus [12] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high-pressure mercury lamp, which was cooled by circulating water or cold methanol. A circulating thermostat bath (Heto CB 11e) was used to provide a constant temperature during the kinetic measurements. Isopropylalcohol was circulated from the thermostat through the heating jacket of the reaction vessel. $Cr(CO)_5(\eta^2\text{-zco})$ was prepared according to the literature procedure [2]a.

2.1. Kinetic measurements

The rate of the displacement reactions of *cis*-cyclooctene, zco, in $Cr(CO)_5(\eta^2\text{-zco})$ by tetracyanoethylene, tcne, at various temperatures was determined by means of FTIR spectroscopy. In order to keep the temperature constant during the kinetic measurements, a Specac Automomatic Temperature Controller P/N 20120 in combination with a circulating thermostat bath, Heto CB 11e, was used. Isopropyl alcohol was circulated from the thermostat through the heating jacket of the reaction vessel.

The kinetic measurements were conducted in toluene solutions in an IR cell with a 0.0320 mm path length with calcium fluoride windows. $Cr(CO)_5(\eta^2\text{-zco})$ (50 mg, 0.165 mmol) was added into the 5 ml solution of 10-fold tcne (1.65 mmol) in toluene containing 5% zco (by volume). The concentrations obtained for the $Cr(CO)_5(\eta^2\text{-zco})$ and for the tcne are 0.033 and 0.331 M, respectively. Since, the substitution reaction is very rapid at room temperature, the tcne solution being in a Schlenk tube was cooled in liquid nitrogen–methanol bath at about −30 °C. It was then transferred into an IR liquid sample cell, which is placed inside the cell holder of the thermostat in which the rest of the reaction mixture is maintained. The reaction rates were determined by following the disappearance of the highest frequency peak of the reactant at 2069 cm^{-1}, because it is the most distinct peak that does not overlap with any peak of the product, and the growth of the highest frequency peak of the product at 2047 cm^{-1}, which also remains well resolved throughout the reaction. Thus the material balance could also be checked at any point of conversion. The observed rate constants were obtained as a result of the graphical evaluation of the data for the substitution reactions in the temperature range of (−5) to 10 °C by an increment of 5 °C.

Kinetic experiments were also performed by varying the concentration of tcne (1-, 5-, 8-, and 10-folds) at all the aforementioned temperatures, −5, 0, 5, and 10 °C, in order to study the dependence of the observed rate constants on the concentration of the entering ligand.

Molar extinction coefficients of $Cr(CO)_5(\eta^2\text{-zco})$ and $Cr(CO)_5(\eta^2\text{-tcne})$ were determined from standard solutions which were prepared by dissolving known amount of pure complexes in toluene. A standard graph was obtained by plotting the absorbance of the highest frequency CO band of the reactant or product versus the concentration of the respective complex in the range of 1×10^{-3}–6×10^{-3} mol l^{-1}. The slope of these lines gave molar extinction coefficients, $\varepsilon = 1415$ l mol^{-1} cm^{-1} at 2069 cm^{-1} for $Cr(CO)_5(\eta^2$-zco) and $\varepsilon = 4562$ l mol^{-1} cm^{-1} at 2047 cm^{-1} for $Cr(CO)_5(\eta^2$-tcne).

3. Results and discussion

The $Cr(CO)_5(\eta^2$-zco) complex (**1**), prepared and identified as described elsewhere [2]a, reacts with tetracyanoethylene (tcne) at room temperature to yield the complex $Cr(CO)_5(\eta^2$-tcne) (**2**) according to the Equation 2:

$$\underset{\mathbf{1}}{Cr(CO)_5(\eta^2 zco)} + tcne \rightarrow \underset{\mathbf{2}}{Cr(CO)_5(\eta^2 tcne)} + zco \qquad (2)$$

The product complex **2** was also isolated and identified by IR and ^{13}C-NMR spectroscopy [5]. In this thermal substitution reaction of the labile complex **1**, zco is replaced by another olefin, tcne, yielding thermodynamically stable complex **2**. The kinetics of the thermal substitution reaction in toluene solution were followed by using the quantitative FTIR spectroscopy at temperatures between −5 and +10 °C. In the ν_{CO} region of the IR spectrum, the absorption bands of **1** at 2069 (s), 1988 (w), 1949 (vs), and 1930 cm^{-1} (sh) are gradually replaced by the new bands of the corresponding product **2** at 2047 (s), 2010 (w), and 1973 cm^{-1} (vs) in the course of the displacement reaction. Also an absorption feature grows in at 2186 cm^{-1}, which is readily attributed to CN stretching of the coordinated tetracyanoethylene [5]. The gradual change in the IR spectrum during the reaction of **1** with tcne at −5 °C in toluene is depicted in Fig. 1 as an example. The observation of nice isosbestic points indicates a straightforward conversion of the reactant into the product without side or subsequent reactions [13]. In other words, there are only two IR absorbing species throughout the reaction. Another point emerging from the inspection of the IR spectra at first glance is that the highest frequency ν_{CO} bands of the reactant and product do not overlap and remain well resolved during the whole reaction. Therefore, these two IR bands are selected to follow the consumption of the reactant and the growth of the product, respectively.

The logarithmic plot of the concentration of the reactant versus time gives a straight line (Fig. 2) for the aforementioned reaction in the presence of 10-fold excess of tcne. This indicates that the displacement of zco from **1** by tcne obeys the pseudo-first order kinetics with a correlation constant greater than 0.99. The slope of the straight line gives the observed rate constant, k_{obs} (s^{-1}), for the pseudo-first-order thermal substitution reaction at the respective temperature. All the observed rate constants obtained for the thermal substitution of zco in **1** by tcne at various temperatures and tcne concentrations are listed in Table 1.

It has been shown that rapid and complete conversion of $Cr(CO)_5(\eta^2$-zco) into $Cr(CO)_6$ occurs upon treatment of an alkane solution of **1** with carbon monoxide and this reaction is significantly retarded if carried out in the presence of an excess of *cis*-cyclooctene [2a]. One can propose a dissociative mechanism involving the facile, reversible loss of the olefinic ligand yielding the $Cr(CO)_5$ species as an intermediate which will be attacked by a nucleophile present in the solution. The question whether a $[Cr(CO)_5(solvent)]$ molecule or coordinatively unsaturated $[Cr(CO)_5]$ complex is the species involved in the further reaction has been addressed through studies of mechanism and catalysis employing photogenerated

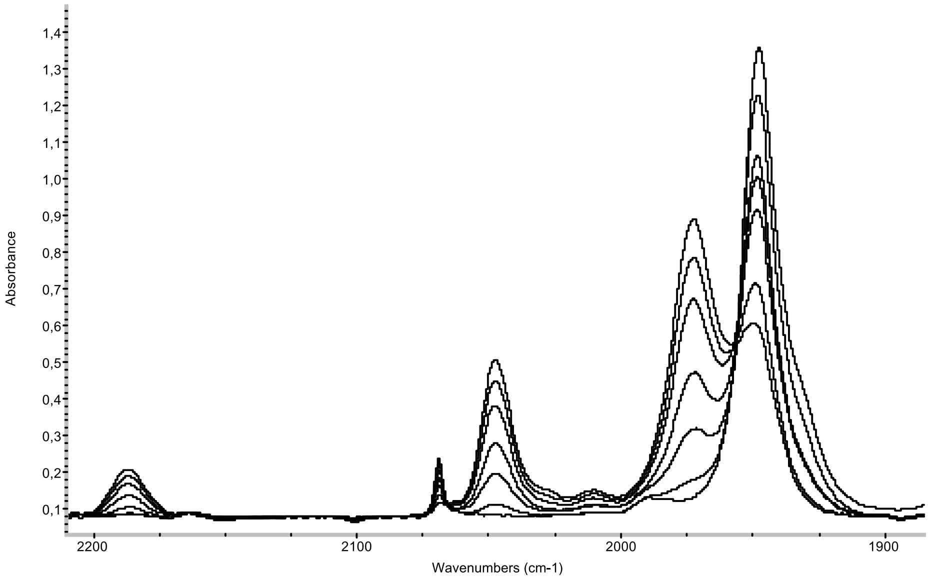


Fig. 1. The FTIR spectra taken in the course of the thermal substitution reaction of **1** with tcne in toluene solution containing 5% b.v. zco at −5 °C. $[tcne]_o/[\mathbf{1}]_o = 10$.

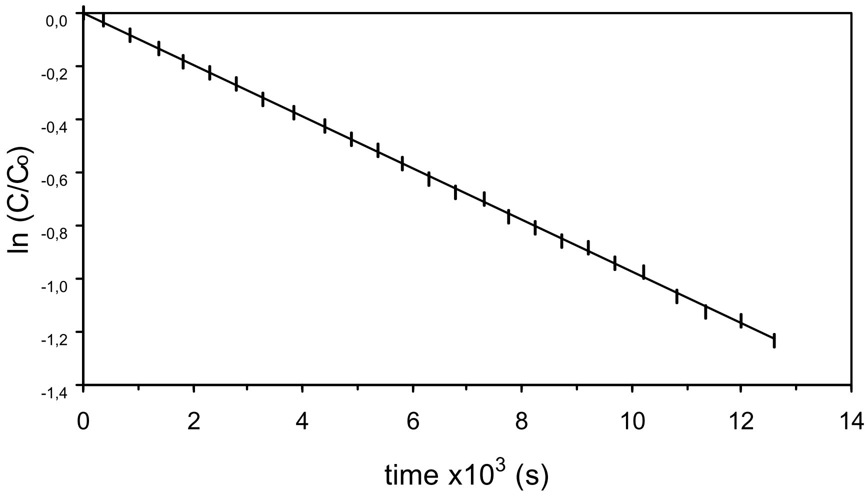
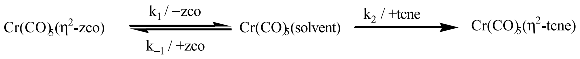


Fig. 2. Plot of the first order kinetics for the substitution reaction of **1** with tcne in toluene solution containing 5% b.v. zco at −5 °C. [tcne]$_o$/[**1**]$_o$ = 10.

Table 1
The observed rate constant values ($k_{obs} \times 10^4$, s^{-1}) obtained for the thermal substitution of zco in the complex **1** by tcne at various temperature (T, in K) and concentrations of teracyanoethylene (tcne, in M)

[tcne] (M)	T (K)			
	268	273	278	283
0.033	0.312	0.482	1.80	4.69
0.066	0.537	0.911	2.93	6.89
0.166	0.869	2.17	4.99	10.8
0.265	0.982	2.26	6.64	14.4
0.331	0.997	2.48	6.86	14.9



Scheme 1. Mechanism proposed for the substitution of Cr(CO)$_5$(η^2-zco) (**1**) with tetracyanoethylene (tcne) in toluene solution.

intermediates [14]. Mechanistic studies have shown that the replacement of the solvent from [Cr(CO)$_5$ (solvent)] intermediate is much slower (nanosecond to millisecond) [15] than the attack of [Cr(CO)$_5$] by solvent (picosecond) [16]. Therefore, it is conceivable that [Cr(CO)$_5$(solvent)] is formed as intermediate upon the reversible, thermal detachment of *cis*-cyclooctene (zco) from Cr(CO)$_5$(η^2-zco) (**1**). This intermediate undergoes solvent replacement by either *cis*-cyclooctene yielding the starting complex **1** or tetracyanoethylene (tcne) forming the product Cr(CO)$_5$(η^2-tcne) (**2**) as shown in Scheme 1.

Assuming a steady-state concentration of the intermediate complex [Cr(CO)$_5$(solvent)], the rate law corresponding to this mechanism can be derived as:

$$-\frac{[\mathrm{Cr(CO)_5}(\eta^2\mathrm{zco})]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{Cr(CO)_5}(\eta^2\mathrm{zco})] \quad (3)$$

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{tcne}]}{k_{-1}[\mathrm{zco}] + k_2[\mathrm{tcne}]}$$

Fig. 3a shows how the observed rate constant varies with the concentration of tcne at different temperatures. At all temperatures, the observed rate constant value increases with the increasing concentration of the entering ligand, however, approaching an asymptotic value at high concentrations. This implies that the observed rate constant will have a saturation limit at high concentrations of the entering ligand. This limiting value is the rate constant k_1 for the displacement of olefin ligand in **1** as shown below:

$$\lim_{[\mathrm{tcne}]\to\infty} k_{\mathrm{obs}} = \lim_{[\mathrm{tcne}]\to\infty}\left(\frac{k_1 k_2[\mathrm{tcne}]}{k_{-1}[\mathrm{zco}] + k_2[\mathrm{tcne}]}\right) = k_1 \quad (4)$$

Due to the limited solubility of tetracyanoethylene in toluene, it is not possible to increase the tcne concentration beyond the 10-fold excess. Therefore, the saturation limit of the observed rate constant could not be achieved by working at available concentration of tcne (not sufficiently high). However, the Equation 3 can be arranged into a form (Equation 5), which will permit us to estimate the k_1 value from the present data obtained by working at available concentration of tcne.

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2}\cdot\frac{[\mathrm{zco}]}{[\mathrm{tcne}]} \quad (5)$$

Plots of $1/k_{obs}$ versus 1/[tcne] give straight lines (Fig. 3b) as expected from the Equation 5. The k_1 values, estimated from the intercept of the extrapolated lines in Fig. 3b, are 1.44×10^{-4}, 5.93×10^{-4}, 9.74×10^{-4}, and 1.82×10^{-3} s^{-1} at 268, 273, 278, and 283 K, respectively.

The k_1-values at four different temperatures are evaluated for the activation parameters of the dissocia-

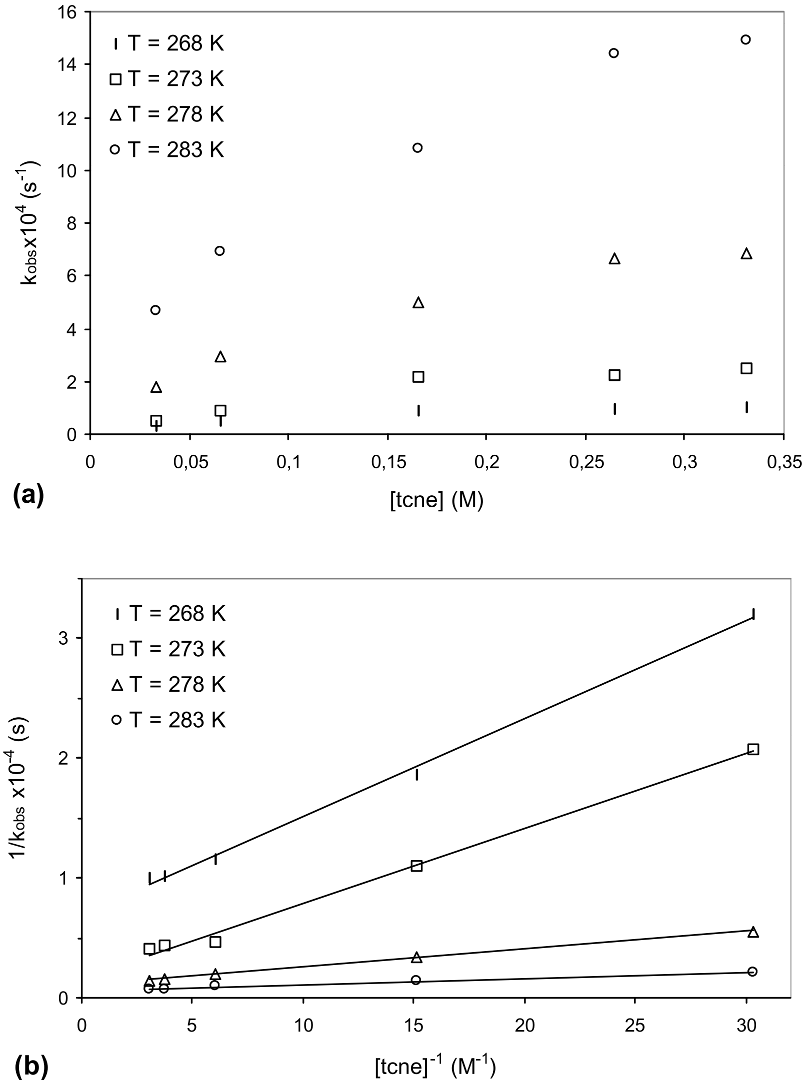


Fig. 3. Variations in the observed rate constant with the concentration of the entering ligand, tcne, for the substitution reaction of $Cr(CO)_5(\eta^2$-zco) (**1**) with tcne in toluene solution containing 5% b.v. zco at various temperatures. $[\mathbf{1}]_o = 0.033$ M. (a) the plots of k_{obs} vs. [tcne], (b) the plots of the reciprocal k_{obs} vs. the reciprocal [tcne]. At all temperatures, the k_{obs} vs. [tcne] plot shows that the observed rate constant approaches a saturation limit at high concentrations of the entering ligand. The saturation limit can be obtained from the intercept of the extrapolated lines in (b).

tion of zco from the complex **1** (Fig. 4). The enthalpy of activation and entropy of activation were found to be $\Delta H^\circ = 100 \pm 3$ kJ mol^{-1} and $\Delta S^\circ = 59 \pm 3$ J K^{-1} mol^{-1}, respectively. The large positive value found for the entropy of activation is consistent with the dissociative nature of the rate determining k_1 step. For a dissociative reaction like the displacement of zco from the complex **1** the enthalpy of activation is expected to be close (ideally equal) to the metal–ligand bond dissociation enthalpy [17]. The exact value of the chromium–zco bond dissociation enthalpy has not been determined so far. However, it can be estimated from the enthalpy change ($\Delta H = -60$ kJ mol^{-1})[18] for the reaction, $Cr(CO)_5(solvent) + zco \rightarrow Cr(CO)_5(\eta^2$-zco) + solvent in n-heptane solution, and bond dissociation enthalpy of chromium–solvent bond ($\Delta H = 42$ kJ mol^{-1} for n-heptane) [19]. The estimated value of 102 kJ mol^{-1} for the chromium–zco bond dissociation enthalpy is very similar to that of chromium–ethene bond dissociation energy (104 kJ mol^{-1}) [20]. Thus, the closeness of the enthalpy of activation to the chromium–olefin bond dissociation energy is consistent with the dissociative nature of the displacement of zco from $Cr(CO)_5(\eta^2$-zco).

The second order rate constant k_{-1} for the reverse reaction of the $Cr(CO)_5$(solvent) complex with *cis*-cyclooctene has already been reported to be 1.4×10^7 l mol^{-1} s^{-1} in the case of n-heptane at room temperature, determined by using time-resolved photoacoustic calorimetry [18]. Since the same reaction with *trans*-cyclooctene (at least, sterically quite different from *cis*-cyclooctene) has also been found to have a similar rate constant value (1.7×10^7 l mol^{-1} s^{-1}) [18], it is conceivable that the rate constant for the displacement

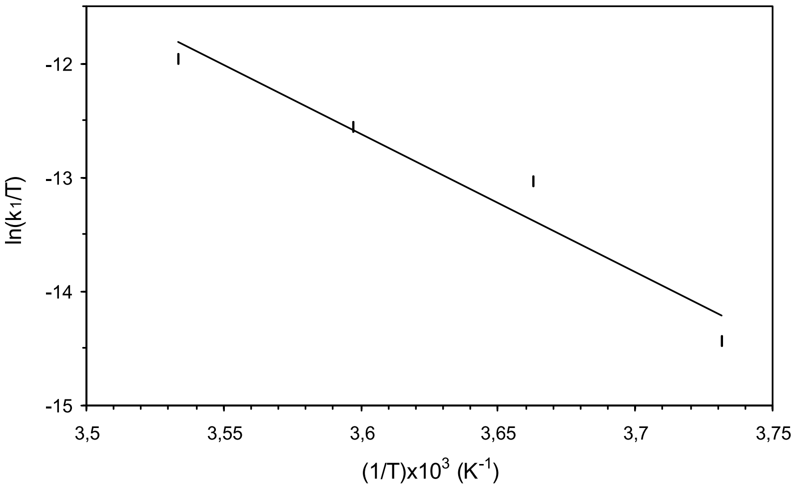


Fig. 4. Eyring plot for the displacement of zco in $Cr(CO)_5(\eta^2\text{-zco})$ (**1**) as the rate determining step (k_1) in the substitution reaction of **1** with tcne in toluene solution containing 5% b.v. zco at various temperatures. $[\mathbf{1}]_o = 0.033$ M.

of solvent in the $Cr(CO)_5$(solvent) complex by an olefin does not strongly depend on the nature of the olefin ligand. Therefore, the k_{-1} and k_2 steps in Scheme 1 are expected to have comparable values for the second order rate constant for the displacement of solvent in the $Cr(CO)_5$(solvent) complex by an olefin, *cis*-cyclooctene or tetracyanoethylene, respectively. The large values of the second order rate constants, k_{-1} and k_2, compared with the rate determining k_1 step, implies that the replacement of solvent in the $Cr(CO)_5$(solvent) complex by an olefinic ligand (zco or tcne) is much faster than the displacement of the zco ligand in **1** by a solvent molecule, especially, in the presence of excess olefin. Thus, the validity of the pseudo-first order conditions is established.

4. Conclusion

The complex $Cr(CO)_5(\eta^2\text{-}cis\text{-cyclooctene})$, **1**, is stable enough at room temperature in solid state, however, gradually decomposes with formation of $Cr(CO)_6$ in solution above −40 °C unless an excess of *cis*-cyclooctene is present. The lability of the complex has made it a useful $Cr(CO)_5$ transfer reagent. The replacement of *cis*-cyclooctene (zco) in the complex by another monodentate olefin ligand is of particular interest. Of the two olefins yielding, the $Cr(CO)_5(\eta^2\text{-olefin})$ as the sole product of the photosubstitution of the parent hexacarbonylchromium(0), one (tetracyanoethylene) was used to replace the other (*cis*-cyclooctene). This is the first kinetically studied substitution reaction of a pentacarbonylmonoolefinmetal(0) complex of Group 6. The complex **1** undergoes a replacement reaction with tetracyanoethylene (tcne) in toluene solution at temperatures near 0 °C at an appreciable rate. Quantitative FTIR spectroscopy was used to study the kinetics of this substitution reaction. A first order dependence of reaction rate on the concentration of $Cr(CO)_5(\eta^2\text{-zco})$ was observed under the pseudo-first order conditions. The observed rate constant, k_{obs}, increases with the increasing concentration of tcne and approaches to a saturation limit at high concentration. This limiting value of k_{obs} is the rate constant k_1 for the displacement of zco from **1** forming the intermediate complex $Cr(CO)_5$(solvent). That this rate-determining step is dissociative was supported by the large positive value of activation entropy and large value of activation enthalpy, which is close to the chromium–zco bond dissociation energy. The dissociative nature of the reaction is readily attributed to the small radius of chromium, and the presence of quite bulky ligand, *cis*-cyclooctene, which stericlly hinders the seven coordination sphere of chromium. The *cis*-cyclooctene ligand in $Cr(CO)_5(\eta^2\text{-zco})$ can be replaced by another olefin like tetracyanoethylene in toluene solution at an appreciable rate even at temperatures near 0 °C and in the presence of excess amount of leaving olefin. This shows that the $Cr(CO)_5(\eta^2\text{-zco})$ complex can be used as $Cr(CO)_5$ source for the preparation of the pentacarbonylchromium(0) complexes which are not stable at ambient temperature and requires working at lower temperatures. It would be of interest to extend this type of kinetic study to the dissociation of a range of olefins from $Cr(CO)_5(\eta^2\text{-olefin})$ when these complexes become accessible.

Acknowledgements

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