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The conformational dynamics of dicarbonylcyclopentadienyl(2-oxopropyl)iron(II): An infrared and molecular mechanics study

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Abstract

The conformational dynamics of dicarbonylcyclopentadienyl(2-oxopropyl)iron(II) have been examined using FT-IR and can be attributed to the rotational freedom about the Fe–C_α and C_α–C_{oxo} bonds. ^{13}C–CO labelling experiments were used to identify the major conformer in an *n*-pentane solution of the compound. The dynamic processes were modelled using the molecular mechanics force field MMX and the results of which corroborate the spectroscopic evidence. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dicarbonylcyclopentadienyl(2-oxopropyl)iron(II); Conformational dynamics; FT-IR; Molecular mechanics

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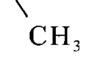
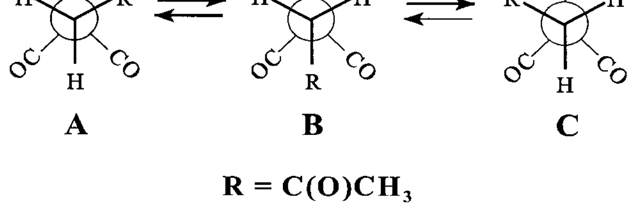
1. Introduction



Fp-2-oxopropyl

Dicarbonylcyclopentadienyl(2-oxopropyl)iron(II), (abbreviated Fp-2-oxopropyl, where Fp = (η^5-C_5H_5)Fe$(CO)_2$), an example of an η^1-oxaallylmetal complex, was first reported in 1964 [1]. No discussion of the conformational dynamics of this structurally simple compound was made at that time. The potential for observing conformational dynamics in Fp-2-oxopropyl can be readily recognized when this compound is represented by the general formula Fp-CH_2R, where R = C(O)CH_3. Newman projections about the Fe–C_α bond of Fp-CH_2R illustrate the three rotamers that result from rotation about this bond, of which conformers A and C are degenerate (Scheme 1). Compounds of this general formula, where R = alkyl or aryl, have been observed to exist in solution in an equilibrium of two or more possible rotamers due to the rotation about the Fe–C_α bond [2]. By analogy, rotational isomerism should also be observed for Fp-2-



Scheme 1. The three rotamers resulting from rotation about the Fe–C_α bond.

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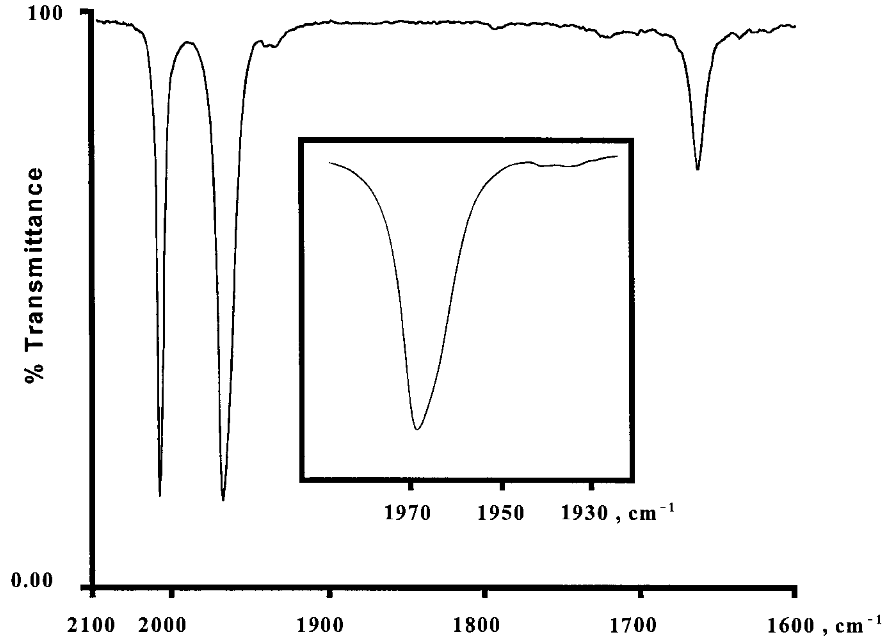


Fig. 1. IR spectrum of Fp-2-oxopropyl in the ν_{CO} region (*n*-pentane solution).

oxopropyl due to rotation about this bond. Free rotation can also occur about the C_α–C_{oxo} bond of Fp-2-oxopropyl, which increases the conformational complexity of this compound.

The use of IR spectroscopy as a tool for identifying rotational dynamics in transition metal carbonyl compounds is well established [3]. The frequency of absorption of the carbonyl stretching mode, ν_{CO}, is very dependent on the geometry of the compound [4]. When rotational isomerism is active in a transition metal carbonyl compound, the ν_{CO} bands for each rotamer are observed in most cases as distinct peaks. The local symmetry of the $M(CO)_n$ fragment of η^5-cyclopentadienyl transition metal carbonyl compounds determines the number of ν_{CO} bands that will be observed in the IR spectrum [5]. The $Fe(CO)_2$ fragment of Fp-2-oxopropyl has C_{2v} symmetry, and therefore two IR active ν_{CO} bands are expected [6]. Generally, the observation of more than the expected number of ν_{CO} bands in the IR spectrum of a transition metal carbonyl compound is evidence for the presence of rotational isomerism [7].

Our interest in the dynamics of Fp-2-oxopropyl and related compounds stems from our investigation of the reactivity of the co-ordinated η^1-oxaallyl ligand (unpublished results). Knowledge of the conformational preferences and dynamics of the co-ordinated oxaallyl may provide insight into the reactivity of this ligand [8]. We will present a discussion of the spectroscopic evidence for the conformational dynamics of Fp-2-oxopropyl. The molecular mechanics force field MMX will be used to model the conformational process [9]. A combination of these methods will be used to predict the preferred conformer(s) of Fp-2-oxopropyl in solution.

2. Results and discussion

Initial examination of the carbonyl stretching region of the infrared spectrum of Fp-2-oxopropyl, as an *n*-pentane solution, revealed the expected bands for the dicarbonyl [10]. Two very sharp, intense peaks are observed at 2018.8 and 1968.8 cm^{-1}, and are assigned to the symmetric and antisymmetric stretch, respectively, of the two terminal carbonyls (Fig. 1) [1,4]. The oxo carbonyl stretch is observed at 1662.8 cm^{-1}. Closer examination of the terminal carbonyl stretching bands revealed that they are not symmetric about their peak maxima. Low frequency shoulders are observed on both of these bands. The asymmetry is best illustrated by the antisymmetric ν_{CO} band [11] (refer to the insert in Fig. 1). The low frequency shoulders on the main ν_{CO} bands are evidence for the presence of one or more minor conformers of Fp-2-oxopropyl in the *n*-pentane solution of the compound [12]. The shoulders are assigned to the symmetric and antisymmetric ν_{CO} bands of the minor rotamer(s) in solution. Therefore, Fp-2-oxopropyl exists in solution in an equilibrium between a major conformer and one or more minor rotamers. In this case the sizeable difference in the intensity of the main ν_{CO} peaks in comparison with the shoulders indicates that in solution, the equilibrium between exchanging conformers greatly favours one rotamer (vide infra). Two processes can be identified that contribute to the observed rotational isomerism in Fp-2-oxopropyl; rotation can occur about the Fe–C_α bond and the C_α–C_{oxo} bond. Rotational dynamics about the former bond have been identified in Fp–alkyl systems [2,3].

Molecular mechanics has increasingly found application in transition metal chemistry [13]. It provides a fast and reliable method for modelling the conformational dynamics of structures of interest. The rotational dynamics about the Fe–C_α and C_α–C_{oxo} bonds of Fp-2-oxopropyl have been examined both separately and simultaneously using the MMX molecular mechanics force field. The calculations provide an understanding of the ease of rotation about these bonds, and also predict the conformations of the stable conformers.

The structure of Fp-2-oxopropyl was built using the drawing tools within PCMODEL. The structure was optimized without imposing any constraints on the geometry of the compound. The resulting bond lengths and bond angles were in agreement with crystallographic data of analogous Fp systems [14]. Several initial structures of various configurations were examined. The optimization routines converged the majority of the initial structures to one conformer, represented by **A** (Scheme 1). This conformer (**A**) represented the lowest energy structure of the calculated conformations of Fp-2-oxopropyl and was used as the initial structure for further analysis.

The rotational dynamics about the Fe–C_α and C_α–C_{oxo} bonds of Fp-2-oxopropyl were examined. The dihedral driver option within PCMODEL was used to calculate the rotational energy profile about each of these bonds [15]. Initial calculations considered only the rotation about one of these bonds at a time. Final analysis involved the more realistic model, where both of these bonds are rotated simultaneously. Rotation about the Fe–C_α bond was examined first; the resulting curve is illustrated in Fig. 2. The lowest energy conformer on this profile corresponds to rotamer **A** (Scheme 1). The acetyl group resides in the pocket between the Cp ring and one of the terminal carbonyls. This space is sterically less congested than the area between the two carbonyls [16]. The conformation where the acetyl group eclipses the Cp ring corresponds to the overall energy maximum on the curve (Fig. 2). It is 2.2 kcal mol^{-1} higher in energy than conformer **A**. This value represents the calculated barrier to rotation of the acetyl group (R) past the Cp ring. Barriers to rotation of similar magnitude have been calculated for the rotation of the R group past the Cp ring for Fp–CH_2R systems, where R = CH_3, C_6H_5, {*o*-Me}$_2$-C_6H_3 ([2]a).

The rotational energy profile about the C_α–C_{oxo} bond of Fp-2-oxopropyl is illustrated in Fig. 3. The energy maximum on the curve represents the conformation in which the methyl group eclipses the Fe–C_α bond. This places the methyl group in close proximity to the Cp ring hydrogens. Two other features of note on the curve are (1) the overall energy minimum that is located at the bottom of a sharp energy well, and (2) the broad local energy minimum, which can be described as a low energy plateau. The calculations suggest that the degree of rotation about the C_α–C_{oxo} bond is somewhat restricted, such that it only rotates through ca. 100° between the conformer located at the overall energy minimum (**D**) and that located on the low energy plateau (**F**). A small barrier to rotation about the C_α–C_{oxo} bond was calculated (0.8 kcal mol^{-1}), suggesting that the conformers located at these energy minima can easily exchange, as illustrated in Scheme 2.

The rotations about the bonds of interest are not independent of one another and therefore their simultaneous rotation was examined through a two angle dihedral drive calculation [17]. The resulting rotational energy surface is illustrated in Fig. 4. The major feature of this surface is the energy trough that spans the entire range of the dihedral angle examined about the C_α–C_{oxo} bond. This trough represents a pathway for the interconversion of the rotamers **D** and **F** (Scheme 2); the barrier to rotation for this process was calculated to be 0.74 kcal mol^{-1}. This is consistent with the conclusions drawn from Fig. 3. Contained within this trough is the global energy minimum (E_{global}) on this surface. The conformer located at the E_{global} corresponds to **D** of Scheme 2, and is illustrated in Fig. 5 by two Newman projections: one projection about the

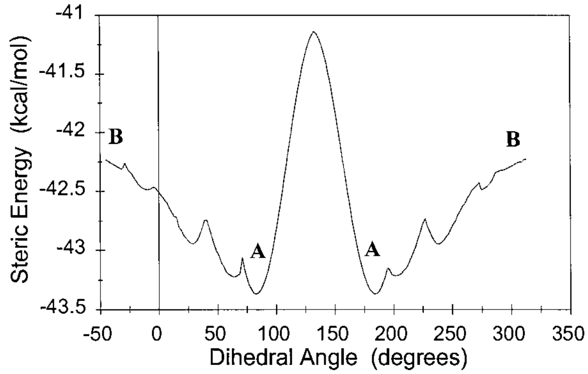


Fig. 2. Rotational energy profile about the Fe–C_α bond of Fp-2-oxopropyl. The dihedral angle is defined as C_{oxo}–C_α–Fe–C_{co}. The labels refer to the Newman projections in Scheme 1.

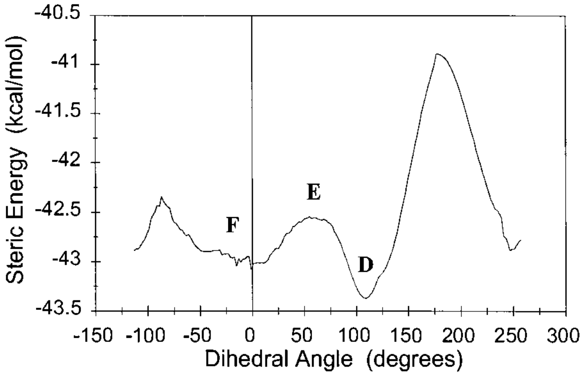
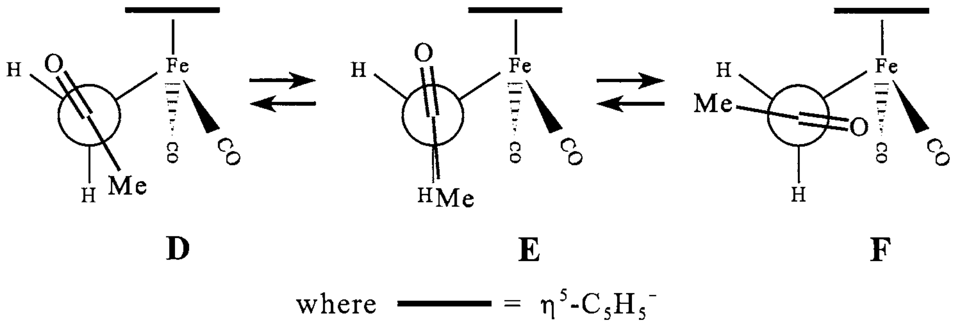


Fig. 3. Rotational energy profile about the C_α–C_{oxo} bond of Fp-2-oxopropyl. The dihedral angle is defined as O_{oxo}–C_{oxo}–C_α–Fe. The labels refer to the Newman projections in Scheme 2.



Scheme 2. Interconversions due to a small barrier to rotation.

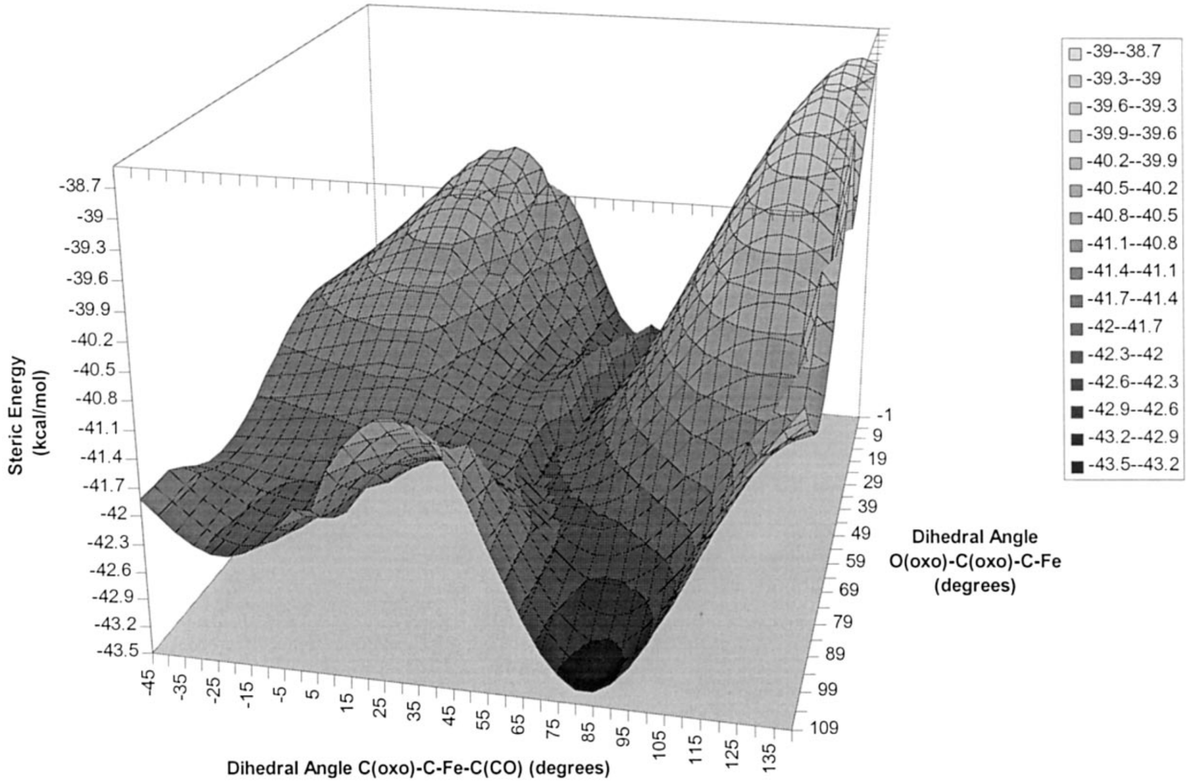


Fig. 4. The potential energy surface for Fp-2-oxopropyl as a function of the dihedral angles C_{oxo}–C_{α}–Fe–C_{co} and O_{oxo}–C_{oxo}–C_{α}–Fe.

Fe–C_{α} bond and the other about the C_{α}–C_{oxo} bond illustrating the dihedral angles C_{oxo}–C_{α}–Fe–C_{co} = 85° and O_{oxo}–C_{oxo}–C_{α}–Fe = 109°, respectively. One other feature of note is the local energy minimum plateau. The general conformation represented here corresponds to **B** of Scheme 1. The steric barrier to rotation for **D**$\rightleftharpoons$**B** was calculated to be 1.32 kcal mol^{-1}.

The molecular mechanics calculations predict that the best conformation for Fp-2-oxopropyl is **D**. Further, two conformers, **B** and **F**, located at the local energy minima on the surface (Fig. 4), have been identified and are energetically accessible to conformer **D**; thus providing a model for the process of rotational isomerism occurring in *n*-pentane solutions of Fp-2-oxopropyl.

The identity of the major rotamer in a solution of Fp-2-oxopropyl was determined by examining the symmetry of the ^{13}C ν_{CO} satellite bands [3]. The ν_{CO} band of the symmetric stretch due to the natural isotopic abundance of ^{13}C is not resolvable from the ^{12}C ν_{CO} band ([6]a), and therefore could not be directly examined. The antisymmetric ^{13}C ν_{CO} is clearly observed at ca. 1937 cm^{-1} as two peaks of equal intensity [18] (Fig. 1). A ^{13}CO-enrichment experiment was conducted and

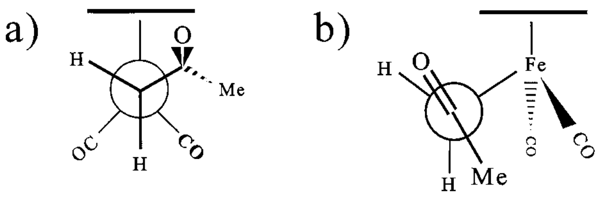


Fig. 5. The Newman projections illustrating the conformer located at the global energy minimum on Fig. 4 about the (a) Fe–C_{α} and the (b) C_{oxo}–C_{α}.

confirmed this assignment [19]. The intensity of not only the antisymmetric ^{13}C ν_{CO} peak, but also that of the symmetric ^{13}C ν_{CO} band increased as a result of the labelling experiment. The latter band could now be resolved. The symmetric and antisymmetric satellite bands were identical in shape and symmetry; each satellite consisted of two bands of approximately equal intensity. The symmetric ^{13}C ν_{CO} bands were observed at 2007.0 and 2001.9 cm^{-1}, and those of the antisymmetric ^{13}C ν_{CO} satellite at 1941.4 and 1935.7 cm^{-1} [6]. The carbonyl groups of rotamer **A** are not equal, and therefore two ^{13}C ν_{CO} satellite bands of equal intensity should be observed [3]. Those of rotamer **B** are equivalent through a symmetry operation, and therefore only a single ^{13}C ν_{CO} satellite band should be observed. Therefore, based on the spectroscopic evidence, the preferred conformer in a solution of Fp-2-oxopropyl has the acetyl group in the pocket between the Cp ring and one of the terminal carbonyl groups (**A** of Scheme 1, where $R = C(O)CH_3$).

The spectroscopic evidence indicates that rotational isomerism is active in the *n*-pentane solution of Fp-2-oxopropyl. Further, the major rotamer of Fp-2-oxopropyl in solution has the acetyl group oriented gauche with respect to the Cp ring. The molecular mechanics calculations have identified the energetically most favorable configuration of Fp-2-oxopropyl as conformer **D**, in agreement with the spectroscopic evidence. Two pathways on the potential energy surface (Fig. 4) have been identified as possible routes for the for the interconversion of **D** with the conformers that are located at local energy minima (**B** and **F**). It is suggested that the majority of the molecules of Fp-2-oxopropyl in solution assume the configuration of conformer **D**, and that an equilibrium exists which interchanges **D** with the minor conformers **B** and **F**. The reactive structural component of the η^1-oxaallyl ligand is the C_α–C_{oxo}–O_{oxo} skeleton. The above conformational analysis of Fp-2-oxopropopyl suggests that the oxaallyl backbone, and in particular the oxo oxygen, adopts a configuration in which it will be exposed to any incoming reactive species, and therefore is available to react with, e.g. electron-deficient π-systems in $[3+2]$ cycloaddition reactions.

Acknowledgements

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[10] Infrared spectra were collected on a Perkin Elmer 1600 Series FTIR operating at a resolution of 2.0 cm^{-1}.

[11] The asymmetry persisted even after repeated purification.

[12] S.C. Mackie, Ph.D. Dissertation, Queen's University, Kingston, Ontario, Canada, 1992. A correlation has been made between the location of the ν_{CO} due to the minor component in solution relative to that of the major conformer for Fp–alkyl systems. If the minor peak is found on the low energy side of the major ν_{CO} then the more populated rotamer in solution conformer **A**. Systems where conformer **B** is preferred the minor ν_{CO} band is on the high energy side of the major band.

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[15] The dihedral driver option of MMX minimizes the energy of a structure while holding one or two dihedral angles fixed. In the case of one bond being driven, the dihedral angle was rotated through 360° at 5° increments and the structure was optimized at each dihedral angle. Several initial conformations were used as input for the single angle dihedral driver calculations. In each case the resulting profiles all had the same basic shape. Any differences that were observed were due to the additional rotational freedom which the other bond of interest contributed. Points identified as anomalous were re-examined and the refined energy value was added to the resulting profile. For comment on this methodology refer to ([13]a) and to A. Beyer, P. Wolschann, A. Becker, G. Buchbauer, J. Mol. Struct. 196 (1989) 371.

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[17] The dihedral driver option was used to rotate the torsional angles C_{oxo}–C_α–Fe–C_{co} and O_{oxo}–C_{oxo}–C_α–Fe about the Fe–C_α and C_α–C_{oxo} bonds, respectively. The symmetry of the Fp moiety allows for the rotation of the Fe–C_α bond through 180°. It was rotated from $-45°$ to $140°$ at 5° increments. This range

rotated the acetyl from a position were it was *anti* with respect to the Cp ring to where it eclipsed the ring system. The second bond was rotated from 109° to −4° at −5° increments. This rotated the C_{α}–C_{oxo} bond as illustrated by Scheme 2. Further rotation of this bond would result in high energy conformations where the methyl group comes into close proximity to a terminal carbonyl and then the Cp ring. Such data points are not of interest since the aim was to identify low energy conformers of Fp-2-oxopropyl.

[18] The intensity of the pair of ^{13}C ν_{CO} satellite bands is ca. 2% that of the ^{12}C antisymmetric ν_{CO}, thus ruling out their assignment as the ^{13}C satellites of the minor rotamer(s) in solution.

[19] The ^{13}CO-enrichment reaction involved presaturating a dilute solution of Fp-2-oxoprpoyl in pentane with $^{13}CO(g)$ (Aldrich). The solution was then photolyzed ($\lambda = 350$ nm) to promote the ^{13}CO-exchange. The progress of the exchange was monitored using IR.