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# INVESTIGATION OF PROTONATION AND ROTATIONAL ISOMERIZATION OF 6-DIMETHYLAMINOFULVENTUNGSTEN TRICARBONYL IN ACIDIC MEDIA BY DYNAMIC $^1$H NMR SPECTROSCOPY

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## Summary

Rotational isomerization of 6-dimethylaminofulventungsten tricarbonyl in media of various acidities has been studied by dynamic $^1$H NMR spectroscopy, and the kinetic parameters of the rotation about the C(6)$\overset{\cdots}{—}$N bond have been determined. The rate of rotation about this bond increases in weakly acidic media and decreases in strongly acidic solutions with respect to that in the parent complex. This dependence indicates that the complex has dual reactivity in protonation, i.e. in weakly acidic media the protonation involves the nitrogen atom, and in highly acidic solutions the tungsten atom. On increasing the acidity of the medium the ammonium form of the complex is converted into the W-protonated complex. A study of deuterium exchange in acidic media has shown that the H or D atom attached to the W atom may be readily exchanged for the deuteron (or the proton, respectively) of the acid, while the H atoms of the cyclopentadienyl ring do not undergo deuterium exchange under the conditions investigated. Protonation involving the Cp ring of the complex was not observed.

## Introduction

In an earlier study we investigated by IR spectroscopy the protonation of 6-dimethylaminofulventricarbonyl chromium (I), -molybdenum (II) and -tungsten (III) in nonaqueous mixtures of acetic and trifluoroacetic acids and in methylene chloride solutions [1]. It was found that I—III are readily protonated at the metal atom at the acidity function $H_0 > -2.51$ for I and $\leqslant +1$ for II and III (eq. 1). In principle, however, the proton may attack the molecules

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of the complexes at other sites: (a) attack may take place at the nitrogen atom

$$[C_5H_4CHN(CH_3)_2]M(CO)_3 \overset{H^+}{\rightleftharpoons} \{[C_5H_4CHN(CH_3)_2]MH(CO)_3\}^+ \qquad (1)$$

leading to formation of the corresponding ammonium salt of the complex (eq. 2) or (b) attack may take place at the cyclopentadienyl ring (Cp) of the complex leading to addition of the proton (eq. 3) and/or to substitution (exchange) of hydrogen atoms in the Cp ring (eq. 4). Considering the results obtained [1],

$$[C_5H_4CHN(CH_3)_2]M(CO)_3 \begin{array}{ll} \xrightleftharpoons{H^+} [C_5H_4CHN^+H(CH_3)_2]M(CO)_3 & (2) \\ \xrightleftharpoons{H^+} [C_5H_5CHN(CH_3)_2]^+M(CO)_3 & (3) \\ \xrightleftharpoons{H^{*+}} [C_5H_{4-n}H^*_nCHN(CH_3)_2]M(CO)_3 & (4) \end{array}$$

it would be expected that at other acidities protonation would involve sites other than the metal atom. Accordingly, we thought it of interest to find out whether the acidity of the medium affects the direction of protonation of complexes I—III.

One of the ways of solving this problem is to study the rotational isomerization about the $C(6) \overset{\cdots}{—} N$ * bond in these compounds in media of various acidities by dynamic $^1H$ NMR spectroscopy, in order to establish the dependence of the kinetic parameters of the rotation about this bond on the acidity. Protonation of the nitrogen atom in the complexes should increase the rotation rate by involving the nitrogen electron pair in the chemical bond, while protonation of other centres (1,3) should increase the degree of double-bond character of the $C(6) \overset{\cdots}{—} N$ fragment and thus decelerate rotation. Data concerning reaction 4 may be obtained by investigating deuterium exchange in acidic media.

The feasilibility of protonation according to eqs. 2—4 in the present work was investigated by a dynamic $^1H$ NMR study of rotational isomerism of 6-dimethylaminofulventungsten tricarbonyl (III) about the $C(6) \overset{\cdots}{—} N$ bond in media of various acidities. The deuterium exchange reaction was also studied.

## Results and discussion

Since nitromethane-*d* was used a solvent, it was necessary to ascertain whether protonation in very acidic solutions of this solvent involves the metal atom as in nonaqueous acids. With this aim the $^1H$ NMR spectra of II and III in nonaqueous $CF_3COOH$ and its nitromethane solutions were recorded. The chemical shifts of hydrogen atoms of the complexes in the $CF_3COOH$/nitromethane mixture were found to be identical to those in nonaqueous $CF_3COOH$. Analysis of the data presented in Table 1 indicates that the signals of all the hydrogen atoms of the complexes are shifted downfield by $\geqslant 0.4$ ppm in the mixture compared with nitromethane, and a signal appears at high field corresponding to the hydrogen atom bonded to the metal ($\delta$ —5.04 ppm for II and $\delta$ —6.86 ppm for III, from TMS) [2,3]. In the case of the tungsten complex III this signal is split, $J(^{183}W—^1H) = 35$ Hz (Fig. 1). The ratio between the integral intensities of the hydrogen atoms signals in the complexes protonated at the metal atom, H(6)/

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* C(6) is the exocyclic carbon atom.

TABLE 1

$^1$H NMR SPECTRA OF $[C_5H_4CHN(CH_3)_2]M(CO)_3$ (II, III) IN NITROMETHANE AND NITROMETHANE/$CF_3COOH$ MIXTURES AT 24°C AND THE COALESCENCE TEMPERATURE OF THE $N(CH_3)_2$ SIGNALS (II, M = Mo; III, M = W)

| | Nitromethane | | Nitromethane-$CF_3COOH$ | |
|---|---|---|---|---|
| | II | III | II | III |
| $T_c$(°C) [a] | 55 | 47 | 67 [b] | 67 [b] |
| δ H(6) (ppm) | 7.71 | 7.75 | 8.57 | 8.54 |
| δ [H(2) + H(5)] (ppm) | 5.62 | 5.55 | 6.12 | 6.28 |
| δ [H(3) + H(4)] (ppm) | 5.48 | 5.44 | 5.94 | 6.10 |
| δ [$N(CH_3)_2$] (ppm) | 3.34 | 3.31 | 3.85 | 3.84 |
| | 3.23 | 3.17 | 3.65 | 3.68 |
| δ(M—H) (ppm) | | | —5.04 | —6.86<br>$J(^{183}W—^1H)$ = 35 Hz |

[a] $T_c$ the coalescence temperature of the $N(CH_3)_2$ signals. [b] Below 67°C no broadening of $N(CH_3)_2$ signals and changes in $\Delta\delta[N(CH_3)_2]$ were observed.

H(2—5)/$N(CH_3)_2$/M—H is 1/4/6/1. Thus, the data previously obtained [1] and that from the present study indicate that complexes II and III are protonated at the metal atom (1) in the mixture of nonaqueous $CF_3COOH$ with nitromethane, as in nonaqueous trifluoroacetic acid.

Under the conditions providing for protonation of complexes II and III at the metal atom in $CD_3NO_2$ the $^1$H NMR signals in the region of absorption of the $N(CH_3)_2$ group do not display any appreciable broadening up to 70°C. In the absence of acid, however, the signals of the $N(CH_3)_2$ groups have a tempera-

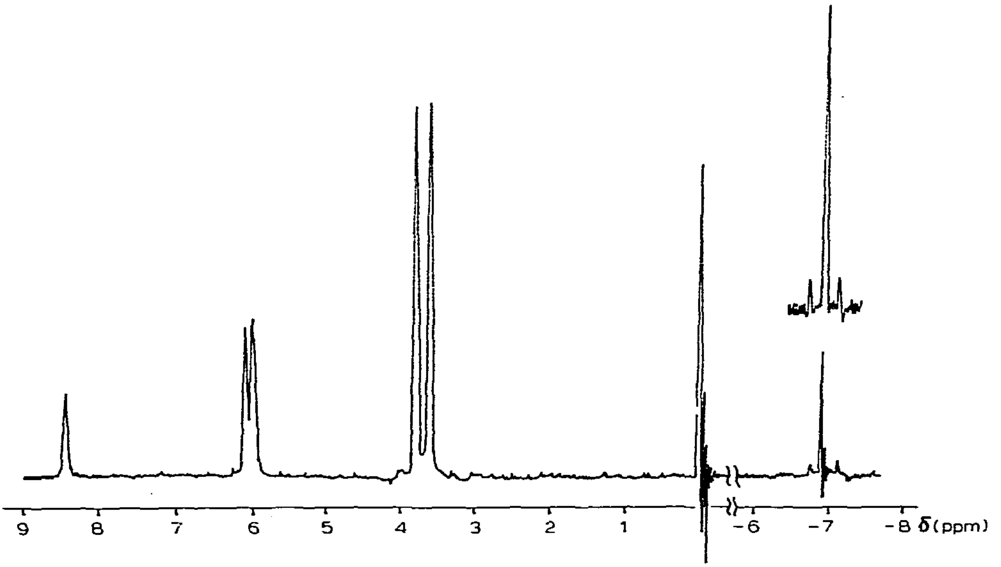
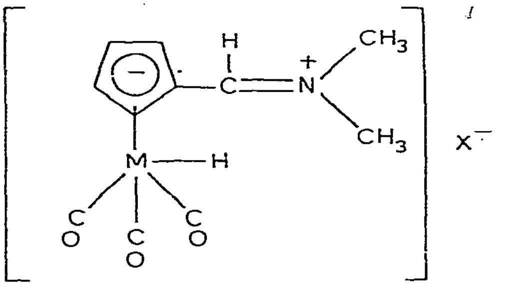


Fig. 1. $^1$H NMR spectrum of $[C_5H_4CHN(CH_3)_2]W(CO)_3$ in nonaqueous $CF_3COOH$ at 24°C.

ture dependence characteristic for rotation about the C=N bond (the coalescence temperatures are 55 and 47°C for II and III, respectively [4]). This evidence suggests that the degree of double-bond character of the C(6)—N bond in the metal-protonated complexes is far greater than in the parent species. Therefore, they should be described by structures IV and V respectively.



( IV , M = Mo ; V, M = W)

Our initial assumption was that protonation at the metal atom should decrease the rate of rotation about the C(6)=N bond. Accordingly, we determined the kinetic parameters of this rotation by dynamic $^1$H NMR spectroscopy for 6-dimethylaminofulventungsten tricarbonyl (III) in nonaqueous mixtures of $CF_3COOH$ and $CD_3COOD$ under conditions ensuring protonation at the metal atom. The rotation rate was monitored by the line shape of signals of the $N(CH_3)_2$ protons. The rotation rate constant was determined by complete line-shape analysis [5], and the energy parameters were inferred from the temperature dependence of the rate constants using the least squares method.

The experimental data in Table 2 suggest that increase in the concentration of trifluoroacetic acid (given here and below in mol % with regard to $CD_3COOD$) and, accordingly, in the acidity of the medium [6], decelerates the rotation and increases the energy parameters of this process. For instance, with an increase of $CF_3COOH$ concentration from 14.35 to 52.33 mol % the rotation rate constant

TABLE 2

PARAMETERS OF ROTATION ABOUT THE C(6)=N BOND OF $[C_5H_4CHN(CH_3)_2]W(CO)_3$ IN NONAQUEOUS MIXTURES OF $CF_3COOH/CD_3COOD$ AND $^1$H NMR SPECTRA (δ, ppm from TMS)

| | Composition of the $CF_3COOH$—$CD_3COOD$ mixture (mol % $CF_3COOH$) | | | | | |
|---|---|---|---|---|---|---|
| | 11.74 | 14.35 | 23.04 | 37.45 | 52.33 | 100 |
| $k_{rot}$(sec$^{-1}$)(24°C) | 8.2 | 7.0 | 1.9 | 0.15 | 0.04 | |
| $\Delta G^{\neq 298}$(kcal mol$^{-1}$) | | 16.2 ± 0.2 | 17.0 ± 0.5 | 18.5 ± 0.2 | 19.3 ± 0.5 | |
| $E_{act}$(kcal mol$^{-1}$) | | 10.3 ± 0.2 | 15.2 ± 0.5 | 23.6 ± 0.4 | 26.2 ± 0.8 | |
| $\Delta H^{\neq}$(kcal mol$^{-1}$) | | 9.65 ± 0.2 | 14.5 ± 0.4 | 21.7 ± 0.4 | 25.6 ± 0.7 | |
| $\Delta S^{\neq}$(e.u.) | | −22.1 ± 0.6 | −8.4 ± 1.5 | 10.6 ± 0.6 | 21.2 ± 3.2 | |
| δH(6) (ppm) | 8.73 | 8.79 | 8.76 | 8.68 | 8.62 | 8.58 |
| δ[H(2) + H(5)] (ppm) | 6.23 | 6.31 | 6.28 | 6.21 | 6.17 | 6.28 |
| δ[H(3) + H(4)] (ppm) | 6.02 | 6.09 | 6.08 | 6.02 | 6.00 | 6.10 |
| δ[$N(CH_3)_2$] (ppm) | 3.75 | 3.88 | 3.83 | 3.81 | 3.78 | 3.84 |
| | 3.61 | 3.69 | 3.66 | 3.61 | 3.62 | 3.68 |
| δ(M—H) (ppm) | — | — | — | −6.89 | −6.86 | −6.86 |

$k_{rot}$ decreases by a factor of 175, the free energy $\Delta G^{\neq\,298}$ increases by 3 kcal mol$^{-1}$, the activation energy $E_{act}$ by 16 kcal mol$^{-1}$, the enthalpy $\Delta H^{\neq}$ by 16 kcal mol$^{-1}$ and the entropy of activation $\Delta S^{\neq}$ by 43 e.u. Figure 2 shows the dependence of $k_{rot}$ on $CF_3COOH$ concentration. The inverse proportional relationship between ln $k_{rot}$ and the concentration of trifluoroacetic acid is described by the' linear equation 5,

$$\ln k_{rot} = 3.76 - 0.14x \tag{5}$$

where $x$ is the mol % $CF_3COOH$ ($\Delta a = \pm 1.01$, $\Delta b = \pm 0.03$ at $P = 0.95$ and $f = 3$; $\Delta a = \pm 1.85$, $\Delta b = \pm 0.06$ at $P = 0.99$ and $f = 3$; $r = 0.992$). At the same time, the rate constant of protonation, $k_{prot}$, is directly proportional to the acidity of the medium (the reaction is pseudo first order) [1]. It seems likely that the rotation rate about the C(6)$\overset{...}{=}$N bond in III would decelerate with increasing protonation rate at the metal atom. Indeed, ln $k_{rot}$ and $k_{prot}$ proved to be in an inverse proportional relationship (Fig. 3) described by a linear equation:

$$\ln k_{rot} = 4.33 - 1.49 \times 10^3\, k_{prot} \tag{6}$$

($\Delta a = \pm 0.04$, $\Delta b = \pm 11$ at $P = 0.95$ and $f = 3$; $\Delta a = \pm 0.06$, $\Delta b = \pm 20$ at $P = 0.99$ and $f = 3$; $r = 0.992$).

Therefore, the decrease in the rotation rate about the C(6)$\overset{...}{=}$N bond in III and the increase in the energy parameters of this process observed with increasing $CF_3COOH$ concentration ($\geqslant$11.74 mol %) in $CF_3COOH/CD_3COOD$ mixtures is due to protonation of the tungsten atom of III and to the increase in the concentration of the resulting complex. It should be noted here that the rotation parameters are effective.

It proved impossible to investigate the protonation of III in nonaqueous $CF_3COOH/CD_3COOD$ mixtures at the a $CF_3COOH$ concentration <11.74 mol % because III is virtually insoluble in such mixtures. The principal possible protona-

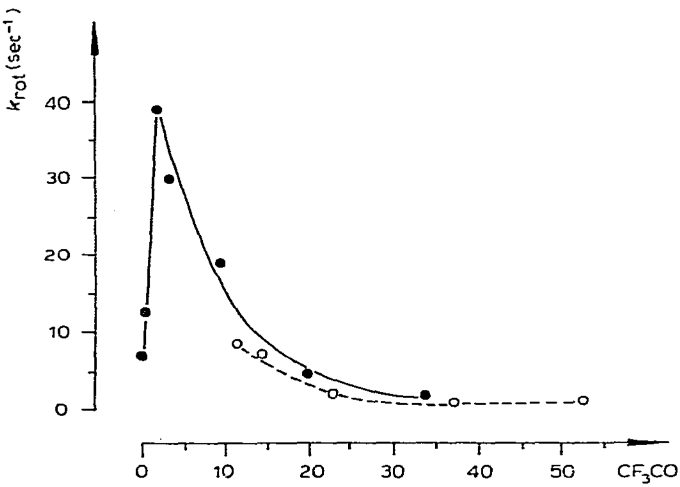


Fig. 2. The dependence of $k_{rot}$ about the C(6)$\overset{...}{=}$N bond of $[C_5H_4CHN(CH_3)_2]W(CO)_3$ on acidity of the medium at 24°C. ●———● in the mixtures of $CF_3COOH/CD_3COOD$ in nitromethane; ○------○ in the nonaqueous mixtures of $CF_3COOH/CD_3COOD$.

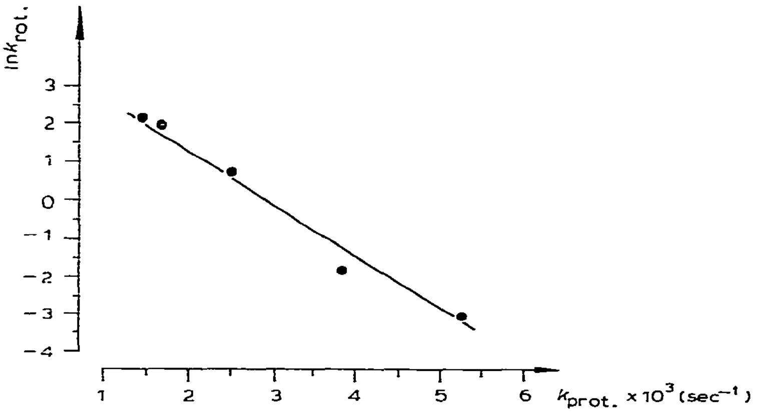


Fig. 3. Dependence of ln $k_{rot}$ about C(6)⋯N bond of $[C_5H_4CHN(CH_3)_2]W(CO)_3$ on $k_{prot}$ in the nonaqueous $CF_3COOH/CD_3COOD$ mixture at 30°C.

tions at other centres of the molecule were therefore examined by determining the kinetics of rotation about the C(6)⋯N bond of III in solutions of substituted acetic acids in nitromethane (Table 3). Addition of $CD_3COOD$ and $ClCH_2COOH$ to the nitromethane solution of III was found to increase the rotation rate constant and to decrease the energy parameters of this process, while the chemical shifts of the proton signals remained essentially unchanged. Such behaviour may be explained by protonation at the nitrogen atom according to eq. 2. (In this case the equilibrium is apparently shifted towards the unprotonated form, and since the protonated form has a short lifetime, the spin-spin coupling constant in the $HN^+(CH_3)_2$ fragment does not manifest itself.) At the same time, addition of stronger acids ($Cl_2CHCOOH$, $Cl_3CCOOH$ and $CF_3COOH$)

TABLE 3

PARAMETERS OF ROTATION ABOUT THE C(6)⋯N BOND OF $[C_5H_4CHN(CH_3)_2]W(CO)_3$ IN SOLUTION OF SUBSTITUTED ACETIC ACIDS IN NITROMETHANE AND $^1$H NMR SPECTRA (δ, ppm from TMS)

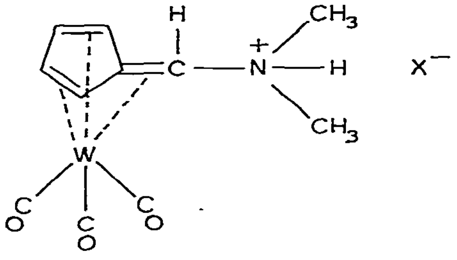
| | Nitromethane | Acid | | | |
|---|---|---|---|---|---|
| | | $CD_3COOD$ | $ClCH_2COOH$ | $Cl_2CHCOOH$ | $CF_3COOH$ |
| $pK_{HA}(CH_3NO_2)$ [a] | | 14.41 [b] | 11.62 | 8.88 | 7.05 |
| $T_c$(°C) | 47 | 40 | 29 | >67 | >67 |
| $k_{rot}$ (sec$^{-1}$) (24°C) | 0.88 | 7.04 | 38.17 [c] | | |
| $\Delta G^{\neq 298}$ (kcal mol$^{-1}$) | 17.2 ± 0.6 | 16.6 ± 0.7 | 15.6 ± 0.7 | | |
| $E_{act}$ (kcal mol$^{-1}$) | 27.0 ± 2.2 | 25.5 ± 0.8 | 12.3 ± 0.7 | | |
| $\Delta H^{\neq}$ (kcal mol$^{-1}$) | 26.8 ± 0.8 | 24.8 ± 0.8 | 11.7 ± 0.7 | | |
| $\Delta S^{\neq}$ (e.u.) | 32.7 ± 6.0 | 27.5 ± 2.0 | −13.0 ± 2.1 | | |
| δH(6) (ppm) | 7.75 | 7.78 | 7.60 | 8.53 | 8.58 |
| δ[H(2) + H(5)] (ppm) | 5.55 | 5.57 | 5.62 | d | 6.29 |
| δ[H(3) + H(4)] (ppm) | 5.44 | 5.47 | 5.55 | d | 6.11 |
| δ[$N(CH_3)_2$] (ppm) | 3.31 | 3.31 | 3.41 | 3.81 | 3.79 |
| | 3.17 | 3.18 | 3.29 | 3.64 | 3.66 |
| δ(M—H) (ppm) | — | — | — | −6.79 | −6.80 |

[a] Cited from ref. 7. [b] For $CH_3COOH$. [c] At 29°C. [d] The signals coincide with that of the dichloroacetic acid CH group.

does not lead to appreciable broadening of the $N(CH_3)_2$ proton signals up to 70°C. This fact, along with the downfield shift of the proton signals and the appearance of a signal from a proton attached to W, indicates that protonation involves the tungsten atom.

The effect of the acidity of the medium on the direction of protonation of III was studied in detail for nitromethane solutions of nonaqueous $CF_3COOH/CD_3COOD$ over a wide range of $CF_3COOH$ concentrations (from 0 to 33.06 mol %) (Table 4). An initial increase in acidity results in increase in the rotation rate about the C(6)$\overset{\dots}{=}$N bond and decrease in the energy parameters of this process, while a further increase in acidity gives an opposite effect (Fig. 2). In this case the signals of all the hydrogen atoms in the $^1$H NMR spectra are shifted downfield in relation to the initial solution in nitromethane, and a signal from a hydrogen atom attached to W appears ($\delta$ —6.80 ppm). In the solution containing 2.09 mol % $CF_3COOH$ the rotation rate is 44 times higher than in the initial nitromethane solution of III, and the energy parameters decrease as follows: $\Delta G^{\neq 298}$ by 2 kcal mol$^{-1}$, $E_{act}$ by 23 kcal mol$^{-1}$, $\Delta H^{\neq}$ by 24 kcal mol$^{-1}$ and $\Delta S^{\neq}$ by 74 e.u. Further increase of $CF_3COOH$ concentration up to 33.06 mole % caused a decrease of the rotation rate by a factor of 48 and the energy parameters increased: as follows $\Delta G^{\neq 298}$ by 2 kcal mol$^{-1}$, $E_{act}$ by 11 kcal mol$^{-1}$, $\Delta H^{\neq}$ by 11 kcal mol$^{-1}$ and $\Delta S^{\neq}$ by 28 e.u.

The observed dependence of the magnitudes of the rotation barriers on the nature of the medium indicates unambiguously that in weakly acidic solutions 6-dimethylaminofulventungsten tricarbonyl(III) is protonated at the nitrogen atom. In this case the nitrogen lone electron pair is involved in a chemical bond with the proton. This results in the disappearance of the double-bond character between the C(6) and N atoms, and in an increase in the observed rotation rate about the C(6)$\overset{\dots}{=}$N bond. Thus the structure corresponding to the nitrogen-protonated complex is VI.



(VI)

In highly acidic nitromethane solutions, as in nonaqueous $CF_3COOH/CD_3COOD$, protonation at the tungsten atom in III involves an inversly proportional relationship between ln $k_{rot}$ and the $CF_3COOH$ concentration:

$$\ln k_{rot} = 3.94 - 0.12x \qquad (7)$$

where $x$ is mol % of $CF_3COOH$ ($\Delta a = \pm 0.58$, $\Delta b = \pm 0.03$ at $P = 0.95$ and $f = 3$; $\Delta a = \pm 1.07$, $\Delta b = \pm 0.06$ at $P = 0.99$ and $f = 3$; $r = 0.997$). Comparison of regression equations 5 and 7 by verifying the hypotheses concerning residual dispersions according to Fisher's $F$-criterion and values of regression constants

TABLE 4

PARAMETERS OF ROTATION ABOUT THE C(6)$\overset{\cdots}{-}$N BOND OF $[C_5H_4CHN(CH_3)_2]W(CO)_3$ IN SOLUTIONS OF $CF_3COOH/CD_3COOD$ IN NITROMETHANE AND $^1H$ NMR SPECTRA ($\delta$, ppm from TMS)

| | Nitromethane | Composition of the $CF_3COOH/CD_3COOD$ mixture (mol % $CF_3COOH$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 0.61 | 2.09 | 3.24 | 9.64 | 19.61 | 33.06 | 100 |
| $T_c$(°C) | 47 | 40 | 33 | 2 | 24 | | 41 | 60 | >67 |
| $k_{rot}$(sec$^{-1}$) (24°C) | 0.88 | 7.03 | 12.53 | 39.06 | 29.94 | 19.2 | 4.1 | 0.82 | |
| $\Delta G^{\neq 298}$(kcal mol$^{-1}$) | 17.2 ± 0.6 | 16.8 ± 0.8 | 15.9 ± 0.7 | 15.3 ± 0.7 | | | 16.4 ± 0.2 | 17.5 ± 0.4 | |
| $E_{act}$(kcal mol$^{-1}$) | 27.0 ± 2.2 | 23.5 ± 1.8 | 15.2 ± 1.0 | 3.7 ± 0.36 | | | 17.5 ± 1.2 | 14.2 ± 0.4 | |
| $\Delta H^{\neq}$(kcal mol$^{-1}$) | 26.8 ± 2.2 | 22.9 ± 1.8 | 14.6 ± 1.0 | 3.1 ± 0.31 | | | 16.9 ± 1.2 | 13.6 ± 0.4 | |
| $\Delta S^{\neq}$(e.u.) | 32.7 ± 6.0 | 22.5 ± 6.0 | −4.4 ± 4.5 | −40.8 ± 0.6 | | | 1.5 ± 2.0 | −13.2 ± 1.1 | |
| $\delta$H(6) (ppm) | 7.75 | 7.72 | 7.42 | 7.41 | 8.34 | | 8.58 | 8.62 | 8.58 |
| $\delta$[H(2) + H(5)] (ppm) | 5.55 | 5.54 | 5.56 | 5.54 [a] | 6.06 | 6.24 | 6.24 | 6.29 | 6.29 |
| $\delta$[H(3) + H(4)] (ppm) | 5.44 | 5.44 | 5.48 | | 6.01 | 6.09 | 6.10 | 6.17 | 6.11 |
| $\delta[N(CH_3)_2]$ (ppm) | 3.31 | 3.26 | 3.28 | 3.70 [b] | 3.70 | 3.78 | 3.86 | 3.90 | 3.79 |
| | 3.17 | 3.13 | 3.16 | 3.63 [b] | 3.63 | 3.67 | 3.66 | 3.71 | 3.66 |
| | | | | 3.22 [a] | | | | | |
| $\delta$(M—H) (ppm) | — | — | — | — | — | — | — | — | −6.80 |

[a] Signals of the N-protonated complex. [b] Signals of the W-protonated complex.

and coefficients according to Student's *t*-criterion [8] has shown that deviations of the regression straight lines from each other are of a random nature. This means that in nonaqueous $CF_3COOH/CD_3COOD$ mixtures and in their nitromethane solutions at $CF_3COOH$ concentrations $\geqslant$2.09 mol %, the rotation rates about the C(6)$\overset{\cdots}{-}$N bond in III are the same as the same concentrations of $CF_3COOH$ in solution.

It may thus be concluded that, depending on the acidity of the medium, the protonation of III yields two different series of the derivatives, either V or VI, which means the direction of the attack of the protons depends on their concentration. This conclusion was confirmed by data on the kinetics of rotation about the C(6)$\overset{\cdots}{-}$N bond in III for nitromethane solutions of $CF_3COOH$ with various acid/III molar ratios. The nature of the observed variation of kinetic parameters of the rotation with acidity is retained here (Table 5). In this case too, an increase in $CF_3COOH$ concentration (i.e. the $CF_3COOH$/III molar ratio) leads first to an increase in the rotation rate about the C(6)$\overset{\cdots}{-}$N bond and to a decrease in the energy parameters of this process, while a further increase in concentration has an opposite effect.

The $^1H$ NMR spectrum of III at a molar ratio $CF_3COOH$/III = 5.5 shows averaged signals of III and of its ammonium form VI ($\delta(C_5H_4)$ = 5.68 ppm, $\delta[N(CH_3)_2]$ = 3.36 ppm from TMS) as well as averaged signals of III and its W-protonated form V ($\delta(C_5H_4)$ = 6.47 ppm, $\delta[N(CH_3)_2]$ = 3.71 ppm from TMS). All the signals are broadened (Fig. 4). At higher $CF_3COOH$ concentrations the spectrum exhibits only narrow signals belonging to protons of V.

Gradual addition of nonaqueous $CF_3COOH$ to the solution of III in $CH_3COOH$/nitromethane at room temperature brings about similar changes in the spectra (Fig. 5). On addition of $CF_3COOH$ to the initial solution of III the signals of the protons of the parent complex III ($\delta$(CH) = 7.73 ppm, $\delta(C_5H_4)$ = 5.62, 5.52 ppm, $\delta$ $[N(CH_3)_2]$ = 3.78, 3.50 ppm from TMS) are broadened and shifted downfield.

TABLE 5

PARAMETERS OF ROTATION ABOUT THE C(6)$\overset{\cdots}{-}$N BOND OF $[C_5H_4CHN(CH_3)_2]W(CO)_3$ IN SOLUTIONS OF $CF_3COOH$ IN NITROMETHANE AND $^1H$ NMR SPECTRA ($\delta$, ppm from TMS)

| | Nitromethane | $CF_3COOH$/complex molar ratio | | | |
|---|---|---|---|---|---|
| | | 1.6 | 5.5 | 27 | 82 |
| $T_c$(°C) | 47 | 47 | 24 | 30 | >67 |
| $k_{rot}(sec^{-1})$ (24°C) | 0.88 | 1.22 | 39.06 | 10.3 | |
| $\Delta G^{\neq 298}$(kcal $mol^{-1}$) | 17.2 ± 0.6 | 17.2 ± 0.6 | 15.3 ± 0.7 | 15.9 ± 1.0 | |
| $E_{act}$(kcal $mol^{-1}$) | 27.0 ± 2.2 | 25.8 ± 2.4 | 11.8 ± 1.8 | 15.1 ± 1.0 | |
| $\Delta H^{\neq}$(kcal $mol^{-1}$) | 26.8 ± 2.2 | 25.2 ± 2.4 | 11.2 ± 1.8 | 14.5 ± 1.0 | |
| $\Delta S$(e.u.) | 32.7 ± 6.0 | 26.8 ± 3.0 | —13.6 ± 5.0 | —4.8 ± 3.0 | |
| $\delta$H(6) (ppm) | 7.75 | 7.86 | | 8.56 | 8.54 |
| $\delta$[H(2) + H(5)] (ppm) | 5.55 | 5.67 | 6.47 [a]<br>5.68 [b] | 6.28 | 6.28 |
| $\delta$[H(3) + H(4)] (ppm) | 5.44 | 5.52 | | 6.14 | 6.10 |
| $\delta[N(CH_3)_2]$ (ppm) | 3.31<br>3.17 | 3.35<br>3.19 | 3.71 [a]<br>3.36 [b] | 3.84<br>3.66 | 3.84<br>3.68 |
| $\delta$(M—H)(ppm) | — | — | — | — | —6.79 |

[a] Signals of the W-protonated complex. [b] Signals of the N-protonated complex.

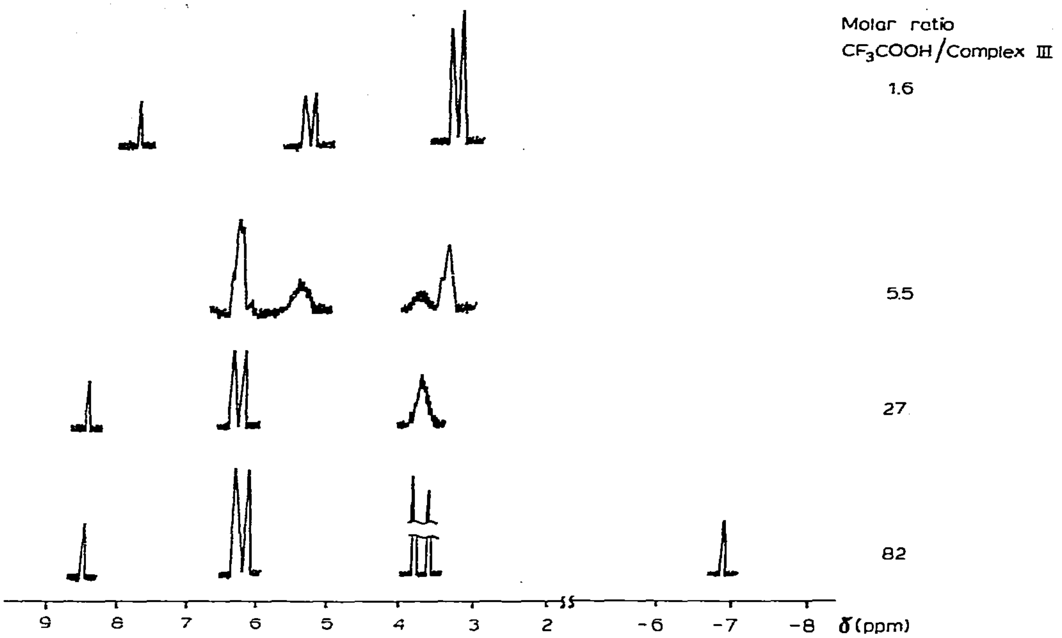


Fig. 4. $^1H$ NMR spectra of $[C_5H_4CHN(CH_3)_2]W(CO)_3$ (III) in the solutions of $CF_3COOH$ in nitromethane at 24°C.

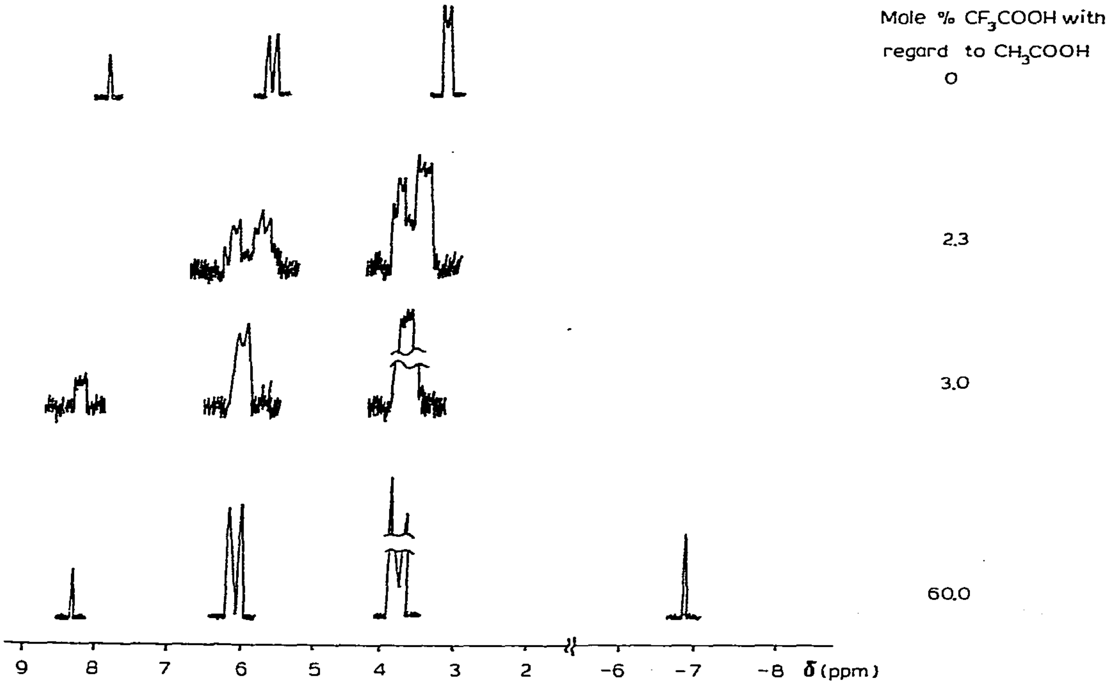
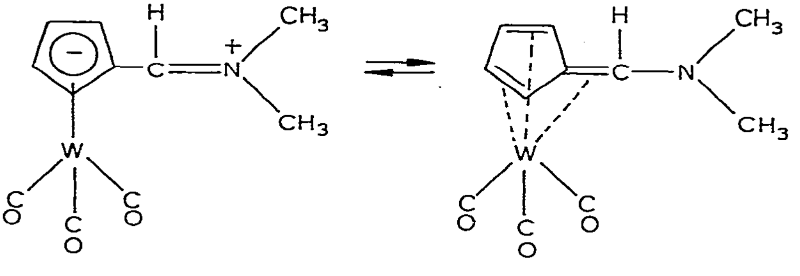


Fig. 5. $^1H$ NMR spectra of $[C_5H_4CHN(CH_3)_2]W(CO)_3$ in $CF_3COOH/CH_3COOH$ mixtures in nitromethane at 24°C.

At 2.3 mol % $CF_3COOH$ the signals belonging both to the ammonium form VI and to the W-protonated complex V ($\delta(C_5H_4) = 6.24$—$5.24$ ppm, $\delta[N(CH_3)_2] = 3.78, 3.50$ ppm from TMS) appear. On increasing the $CF_3COOH$ concentration in the same solution up to 3 mol % the signals of the N-protonated complex disappear, and the signals of V become narrower and shifted further downfield ($\delta(CH) = 8.40$ ppm, $\delta(C_5H_4) = 5.87$ ppm, $\delta[N(CH_3)_2] = 3.73$ ppm from TMS). Finally, at 60 mol % of $CF_3COOH$ the spectrum shows only signals belonging to V ($\delta(CH) = 8.48$ ppm, $\delta(C_5H_4) = 6.07, 5.98$ ppm, $\delta[N(CH_3)_2] = 3.85, 3.68$ ppm, $\delta(W—H) = -6.8$ ppm from TMS).

These data indicate that with increasing acidity of the medium the ammonium form VI is converted into the W-protonated complex V, and at certain acidities both protonated forms are in dynamic equilibrium with each other. Products of the protonation of 6-dimethylaminofulventungsten tricarbonyl at the nitrogen atom (VI) and at the tungsten atom (V) have quite different structures. The transformation VI → V therefore involves structural changes which may be explained by a transfer of the reaction centre in the molecule of the parent complex III at the moment of the reaction or, alternatively, by the existence of tautomeric forms of III, namely $\eta^6$-*N*-dimethylaminofulventungsten tricarbonyl (VIII) and $\eta^5$-6-*N*-dimethylaminoazomethiniumcyclopentadienyltungsten tricarbonyl (VII). However, the dual reactivity of III in protonation reactions cannot be explained unambiguously on the basis of the experimental data obtained.



(VII) (VIII)

$^1H$ NMR spectra of III in nonaqueous $CF_3COOH/CD_3COOD$ and in their nitromethane solutions, as well as in the solutions of substituted acetic acids, give no indication of protonation at the cyclopentadienyl ring according to eq. 3.

The integral intensities of proton signals in $^1H$ NMR spectra of III in various media containing $CD_3COOD$ show that under the experimental conditions studied the substitution of D for the hydrogen atoms of the Cp ring according to eq. 4 does not take place or, at least, is extremely slow with a rate constant less than $10^{-5}$ $s^{-1}$.

In order to establish whether the hydrogen (or deuterium) atom attached to the metal atom in V is capable of exchange with protons of an acid we have studied the deuterium exchange reaction (Table 6) by comparing the integral intensities of the W—H signal in the $^1H$ NMR spectra of V in the nitromethane/$CF_3COOH$ (or $CF_3COOD$) mixture before and after treatment with deuterotrifluoroacetic (or trifluoroacetic) acid at room temperature. It was found that the hydrogen or deuterium atom attached to the W atom can be rapidly (in ~5 minutes) substituted by the deuteron (or the proton, respectively) of the acid,

TABLE 6

DEUTERIUM EXCHANGE AT THE W—H BOND IN $\{[C_5H_4CHN(CH_3)_2]\ WH(CO)_3\}^+$ IN ACIDIC NITROMETHANE SOLUTIONS AT 24°C

| Acid (mol × $10^{-3}$) | | | Acid (mol %) | | Deuterium exchange (%) |
|---|---|---|---|---|---|
| $CF_3COOH$ | $CF_3COOD$ [a] | $CD_3COOD$ | $CF_3COOD$ | $CD_3COOD$ | |
| 1.05 | 1.34 | — | 44.9 | — | 42 |
| 1.05 | 5.40 | — | 67 | — | 58 |
| 1.05 | — | 1.36 | — | 56.4 | 50 |

[a] Content of $CF_3COOD$ in the acid = 80%.

and that the degree of exchange depends on the concentration of the acid. The exchange resulting from treatment of the initial solutions with deuteroacetic (or acetic) acid was also rapid. The hydrogen atoms of the Cp ring of V are not exchanged according to eq. 4: the integral intensity of the Cp ring protons remains constant for several hours after treating the initial solution with deuterotrifluoroacetic or deuteroacetic acid (if the exchange does take place, its rate constant should be less than $10^{-5}$ $s^{-1}$).

In summary, as a result of our studies on the rotational isomerism of 6-dimethylaminofulventungsten tricarbonyl (III) in media of various acidities by dynamic $^1H$ NMR spectroscopy and on the deuterium exchange reaction, we determined the kinetic parameters of rotation about the $C(6)\overset{\cdots}{-}N$ bond in III and demonstrated that (a) the rotation rate about the $C(6)\overset{\cdots}{-}N$ bond, as well as the direction of attack on the complex by the acid proton essentially depend on the acidity of the medium; (b) protonation of III yields two series of derivatives with quite different structures, namely the N-protonated complex in weakly acidic media and the W-protonated complex in strongly acidic media; (c) the ammonium form of complex IV is converted with increasing acidity of the medium into a complex protonated at the metal atom (V); (d) the rotation rate about the $C(6)\overset{\cdots}{-}N$ bond in weakly acidic media (when protonation involves the N atom) increases with respect to that in the parent complex, and decreases in highly acidic media (with protonation at the metal atom); (e) the hydrogen atom attached to the tungsten atom is readily exchanged in acidic media with the deuteron (or the proton) of the acid; (f) no protonation of the Cp ring of III or exchange of the Cp ring hydrogen atoms with the medium takes place under the experimental conditions studied.

The dual reactivity of III with regard to protonation is presumably explained by the existence of two tautomeric forms of the complex, i.e. $\eta^6$-*N*-dimethylaminofulventungsten tricarbonyl (VIII) and $\eta^5$-6-*N*-dimethylazomethiniumcyclopentadienyltungsten tricarbonyl (VII).

## Experimental

Complexes II and III were obtained as reported previously [1]. Nitromethane-$d_3$ and the acids were purified and dried under argon; the solutions were prepared and ampoules filled also under argon.

The $^1H$ NMR spectra were recorded with a RYa 2309 spectrometer at 90

MHz, using TMS as internal standard. The temperature was maintained accurately to ±0.5°C.

The lifetimes of the rotamers of the complexes $\tau$ were estimated by comparing the experimental spectra of the $N(CH_3)_2$ indicator groups with the computed spectra. The difference in the chemical shifts $\Delta\delta[N(CH_3)_2]$, used for calculating the spectra, was found by extrapolating the observed temperature dependences of the given parameters in the absence of transitions to the region of rapid exchange [5]. Computation of the spectra of $N(CH_3)_2$ groups was carried out on a PDP 12 computer using a program composed in Arnold's formalism [9].

*Protonation of III in nonaqueous $CF_3COOH$ and in $CF_3COOH$—$CD_3NO_2$ mixtures (Table 1).* The solutions contained $0.0128 \times 10^{-3}$ mol III and 0.5 ml $CF_3COOH$ or 0.5 ml $CD_3NO_2$ and $1.05 \times 10^{-3}$ mol $CF_3COOH$. Dissolution of III in the $CF_3COOH$-$CD_3NO_2$ mixture at room temperature results in a light yellowish-green solution which in 2—3 minutes becomes dark red. With dissolution at a low temperature (⩽—20°C) the yellowish-green colour does not change for a long time, and the solution becomes red only as the temperature is raised to the room temperature and remains so after repeated cooling to —40°C. On addition of a fresh portion of $CF_3COOH$ to the cooled sample, however, the solution turns yellowish-green once again, turning red in a few minutes. The $^1H$ NMR spectra of the green and the red solutions are identical. In contrast to this behaviour, the yellowish-green colour of the solution of III in nonaqueous $CF_3COOH$ becomes deeper with time but essentially does not change. Highly acidic nitromethane solutions of III are stable for several hours and withstand long-term heating to 70°C. At this temperature the two signals of the Cp ring protons merge into one, the width of the signal remaining the same, while the chemical shifts of other signals do not change. The temperature-induced changes in the spectrum of the Cp ring are reversible, and upon cooling two signals appear again. The distance between them increases with a decrease of temperature.

*Protonation of III in nonaqueous $CF_3COOH$-$CD_3COOD$ mixtures (Table 2).* The solutions contained $0.0128 \times 10^{-3}$ mol III and 0.5 ml of the $CF_3COOH$-$CD_3COOD$ mixture.

*Protonation of III by substituted acetic acids (Table 3).* The solutions contained $0.0128 \times 10^{-3}$ mol III, $1.64 \times 10^{-3}$ mol acid and 0.5 ml $CD_3NO_2$.

*Protonation of III in $CD_3NO_2$ solutions of $CF_3COOH$-$CD_3COOD$ (Table 4).* $3.28 \times 10^{-3}$ mol $CD_3COOD$ and then trifluoroacetic acid were gradually added to the initial nitromethane solution of III ($0.0128 \times 10^{-3}$ mol III and 0.5 ml $CD_3NO_2$) up to 2.09 mol %. For each solution the temperature dependence of the $^1H$ NMR spectrum in the region of $N(CH_3)_2$ groups was investigated. When the $CF_3COOH$ concentration in the sample had increase to 3.24 and 9.64 mol % it was impossible to determine the energy parameters of rotation about the $C(6)\text{---}N$ bond, since above 35°C the spectra displayed irreversible changes indicating decomposition of the complex. Thus, in order to obtain the kinetic parameters of the rotation about the $C(6)\text{---}N$ bond in solutions containing ⩾9.64 mol % $CF_3COOH$, new samples were prepared for each concentration of $CF_3COOH$. In all these cases the solutions also contained $0.0128 \times 10^{-3}$ mol III, $3.28 \times 10^{-3}$ mol $CD_3COOD$ and 0.5 ml $CD_3NO_2$.

*Protonation of III by trifluoroacetic acid in $CD_3NO_2$ at different molar*

*$CF_3COOH$/III ratios (Table 5).* The initial solution contained $0.0128 \times 10^{-3}$ mol III and 0.5 ml $CD_3NO_2$.

*Protonation of III in $CF_3COOH$-$CH_3COOH$ mixtures in nitromethane at 24°C (Fig. 5).* The initial solution contained $0.0128 \times 10^{-3}$ mol III, $3.28 \times 10^{-3}$ mol $CH_3COOH$ and 0.5 ml $CD_3NO_2$.

*Isotopic exchange of hydrogen attached to the W atom (Table 6).* The initial solutions of V were prepared by dissolving $0.0128 \times 10^{-3}$ mol III in 0.3 ml $CD_3NO_2$ containing $1.05 \times 10^{-3}$ mol $CF_3COOH$ (or $CF_3COOD$).

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