

## THE EFFECT OF MEDIUM ACIDITY ON THE RATE OF PROTONATION OF 6-DIMETHYLAMINOFULVENTRICARBONYL-CHROMIUM, -MOLYBDENUM, -TUNGSTEN AND COMPARISON OF THEIR BASICITY

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### Summary

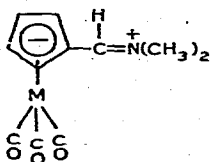
Protonation of 6-dimethylamino-fulvenic complexes of chromium (I), molybdenum (II) and tungsten (III) carbonyls in trifluoroacetic and acetic acid solutions of differing acidity in methylene chloride has been studied using PMR and IR spectroscopy. It has been established that the complexes are protonated at the metal atom and that the protonation rate is linearly dependent on the acidity of the medium. Comparison of the basicities of complexes I–III has shown that their basicity ratio is I/II/III  $\approx$  1/150/1800.

### Introduction

The protonation reaction of  $\pi$ -complexes of transition metals is widely used to study their reactivity [1,2] and, in particular, to compare basicities.

Quantitative determination of the basicities of complexes, however, involves great experimental difficulties. These are caused by a number of reasons, one of which is the absence of an absolute scale of acidity in nonaqueous media. Nevertheless, the study of the protonation rate of isoelectronic isostructural transition metal complexes in media with a known acidity can serve as a possible mean of obtaining quantitative data to characterize the relative basicity of the complexes.

In the present work we investigated the protonation of 6-dimethylamino-fulvenic complexes of chromium (I), molybdenum (II) and tungsten (III)



(I, M = Cr; II, M = Mo; III, M = W)

carbonyls in trifluoroacetic and acetic acid solution with differing values of acidity function  $H_0$  in methylene chloride. It was previously established that a linear dependence exists between the acidity values for nonaqueous acids, such as  $\text{CF}_3\text{COOH}-\text{H}_2\text{SO}_4$  and  $\text{CF}_3\text{COOH}-\text{CH}_3\text{COOH}$ , and their solutions in nonaqueous solvents (methylene chloride, benzene) in the range of  $H_0 = +3.0$  to  $-3.0$  [3] \*. Using these data we investigated the dependence of the protonation rate of complexes I–III in  $\text{CF}_3\text{COOH}-\text{CH}_3\text{COOH}$  solutions in methylene chloride on the acidity of the medium found for the mixtures of nonaqueous acids [4] \*.

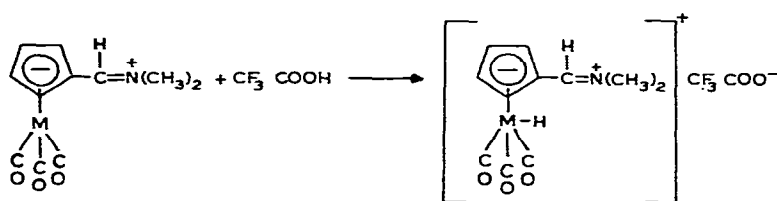
## Results and discussion

The complexes I–III are readily dissolved in trifluoroacetic acid and are practically insoluble in acetic acid.

A high-field signal,  $\tau$  13–18, is observed in PMR spectra of these solutions and is characteristic of a metal-bonded hydrogen atom (M–H bond) [1,2]. The signal is shifted upfield with increasing metal atomic number in the sequence  $\text{Cr} < \text{Mo} < \text{W}$  indicating enhancement of metal-bonded hydrogen shielding. A similar picture was previously observed by Kotz and Pedrotty in a PMR study of the interaction of the Group VI metal carbonyl complexes of triphenylphosphoniumcyclopentadienylide and trifluoroacetic acid [2].

The IR-spectra of complexes I–III in  $\text{CF}_3\text{COOH}/\text{CH}_2\text{Cl}_2$  (1/50) exhibit an increase in CO stretching frequencies of more than  $100\text{ cm}^{-1}$  as compared with those of the initial complexes (Table 1). This change in the IR-spectra is usually observed when protonation of the transition metal  $\pi$ -complexes occurs at the metal atom [1,2,5].

Thus the PMR and IR spectra (Table 1) suggest protonation of the 6-dimethylaminofulvenic complexes of chromium (I), molybdenum (II) and tungsten (III) carbonyls at the metal atom:



I–III

Ia, M=Cr; IIa, M=Mo; IIIa, M=W

When mixtures of acetic and trifluoroacetic acids of differing molar ratios in methylene chloride (acid/ $\text{CH}_2\text{Cl}_2 = 1/50$ ) were used for the protonation of the complexes I–III, IR spectra of solutions with fixed acidity showed an increase of the intensity ratio  $A_{\text{prot.}}/A_{\text{nonprot.}}$  for the CO absorption bands of the protonated and nonprotonated forms of I–III with time. On the other hand, at the same experiment duration an increase of  $A_{\text{prot.}}/A_{\text{nonprot.}}$  ratio was also observed as the medium acidity was increased (Fig. 1).

\* Acidity function values for these solutions must, obviously, differ from the true  $H_0$  values for a mixture of acids without solvent; these values are, however, proportionate.

TABLE 1

IR CO STRETCHING FREQUENCIES FOR I—III AND Ia—IIIa AND <sup>1</sup>H CHEMICAL SHIFTS FOR THE M-H BOND OF Ia—IIIa

Compound	M	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	$\tau(\text{MH})$
$(\text{CH}_3)_2\text{NCHC}_5\text{H}_4\text{M}(\text{CO})_3$	Cr	1910, 1810 <sup>a</sup>	
	Mo	1920, 1800 <sup>a</sup>	
	W	1915, 1800 <sup>a</sup>	
$[(\text{CH}_3)_2\text{NCHC}_5\text{H}_4\text{M}(\text{CO})_3\text{H}]^+$	Cr	2036, 1962 <sup>b</sup>	13.89 <sup>c</sup>
	Mo	2073, 1984 <sup>b</sup>	14.71 <sup>c</sup>
	W	2042, 1960 <sup>b</sup>	17.53 <sup>c</sup>

<sup>a</sup> In KBr. <sup>b</sup> In  $\text{CF}_3\text{COOH}/\text{CH}_2\text{Cl}_2$  (1/50). <sup>c</sup> In  $\text{CF}_3\text{COOH}$ .

So, as the protonation rate of complexes I—III was dependent on the medium acidity, a kinetic investigation of the reaction appeared to be possible under the experimental conditions studied.

Taking 6-dimethylaminofulvenmolybdentricarbonyl (II) as an example we found the protonation reaction to be reversible, since, on the addition of triethylamine to a solution containing the protonated complex only, CO adsorption bands of the parent were again observed in the IR spectrum of the solution formed.

Table 2 sums up the data on the effect of the medium acidity on the protonation of the complexes I—III at a fixed duration of experiment. Complete protonation of 6-dimethylaminofulvenic complexes of chromium (I), molybdenum (II) and tungsten (III) carbonyls has been established to take place at the values of  $H_0 = -3.03$ ,  $-2.7$  and  $-2.03$ , respectively; metal protonation does not take place at  $H_0 = -2.51$ ,  $\leq +1$  and  $+3$  to  $+1$ , respectively. From these data the increase of the basicity of the complexes is in the sequence  $\text{I} < \text{II} < \text{III}$  follows.

Moreover, on the basis of the experimental data obtained, the relative basicity of the complexes can be estimated quantitatively if the rate of protonation of the complexes at the metal is assumed to be directly dependent on their

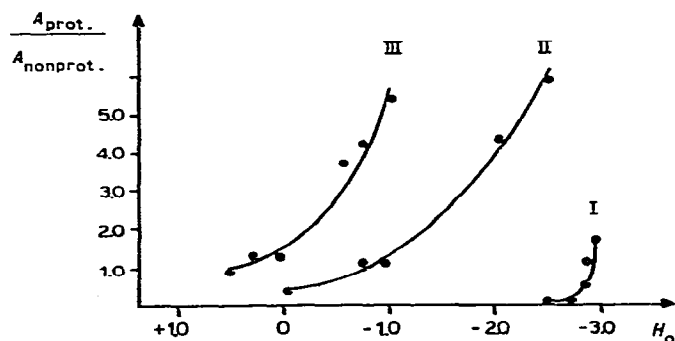


Fig. 1. Ratio of CO-adsorption bands intensities (sym. vibrations) of the protonated and nonprotonated forms of the complex I—III vs. the acidity of the medium ( $H_0$ ) at  $t = \text{const}$ .

TABLE 2  
EFFECT OF MEDIUM ACIDITY ON THE PROTONATION OF COMPLEXES I—III

Compound	M	Protonation		$y = a + bH_0^a$	$H_0^*{}^b$
		complete, $H_0$	absent, $H_0$		
$(CH_3)_2NCHC_5H_4M(CO)_3$	Cr	-3.03	-2.51	$y = -4.42 - 1.78 H_0$	-2.87
	Mo	-2.7	$\leq +1$	$y = 0.22 - 0.69 H_0$	-0.68
	W	-2.03	+3 to +1	$y = 1 - 0.78 H_0$	+0.40

<sup>a</sup>  $y = k_{obs.}t$ . <sup>b</sup>  $H_0^*$  is the function of the acidity of medium at which  $A_{prot.}/A_{nonprot.} = 1$  at  $t = \text{const}$  and  $k_{obs.}^Cr t = k_{obs.}^{Mo} t = k_{obs.}^W t$ .

basicity. A quantitative estimation of the relative basicity of the complexes is made by the comparison of  $H_0$  values at which the concentrations of the protonated and the nonprotonated forms are the same, i.e.,  $A_{prot.}/A_{nonprot.} = 1$  at constant  $t$  (the values of the acidity function are designated as  $H_0^*$ ), and the protonation reaction rate constants ( $k_{obs.}$ ) for the complexes I—III are equal, i.e.,  $k_{obs.}^{Cr} = k_{obs.}^{Mo} = k_{obs.}^W$ . The  $H_0^*$  values for each complex can be calculated from the equation  $k = f(H_0)$  for the dependence of the protonation rate constant on the acidity of the medium.

Under the conditions of the experiment, the acid concentration is much higher than that of the complex, and, therefore, the reaction can be regarded as pseudomonomolecular, of first order kinetics. In this case, the reaction rate constant  $k_{obs.}$  can be calculated from the first-order equation:

$$k_1 = \frac{2.303}{t} \lg \left( \frac{A_0}{A_0 - x} \right) \quad (1)$$

Since  $A_0 = A_{prot.} + A_{nonprot.}$ , equation (1) takes the form of

$$k_1 = \frac{2.303}{t} \lg \left( \frac{A_{prot.}}{A_{nonprot.}} + 1 \right) \quad (2)$$

On the basis of the experimental data on the effect of the medium acidity on the value of the  $A_{prot.}/A_{nonprot.}$  ratio for complexes I—III at a fixed time of experiment ( $t = \text{const}$ ) the  $k = f(H_0)$  relationship is described by the equation of a straight line  $y = a + bx$  (Fig. 2).

The equations of a straight line,  $k_{obs.} t = a + bH_0$  for complexes I—III are given in Table 2. From these equations the values  $H_0^*$  for 6-dimethylamino-fulvenic complexes of chromium (I), molybdenum (II) and tungsten (III) carbonyls are -2.87, -0.68 and +0.40, respectively. Therefore, the ratio of complex basicities is I/II/III  $\approx 1/150/1800$ , and II/III  $\approx 1/12$ .

Thus, the basicity of the chromium complex (I) differs sharply from those of the molybdenum (II) and tungsten (III) complexes, but the difference between the basicities of the complexes of molybdenum (II) and tungsten (III) is not so great.

In order to verify our assumption regarding first order kinetics of the protonation reaction of complexes I—III and to confirm the validity of the equations

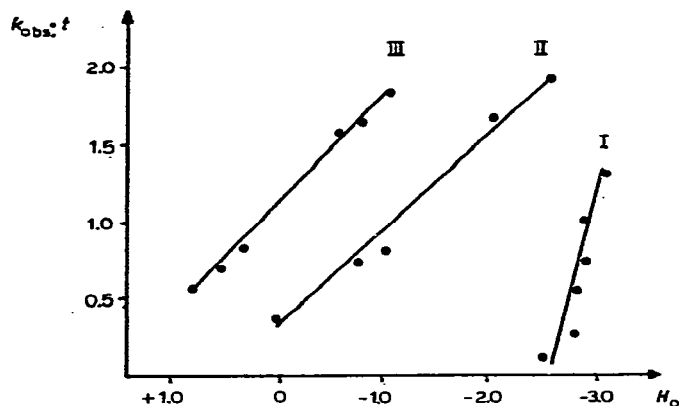


Fig. 2. Protonation rate constant ( $k_{\text{obs.}t}$ ) of the complexes I — III vs. the acidity of medium ( $H_0$ ) at  $t = \text{Const.}$

found for the dependence of the reaction rate constants on the acidity of the medium we undertook an IR study of the protonation kinetics of 6-dimethylaminofulvenmolybdenetricarbonyl (II) at  $H_0 = -0.06$  by following the change of the starting complex concentration.

It was found that i) the reaction is in fact pseudomonomolecular;  $\lg(A_0/(A_0 - x))$  is linearly dependent on time (Fig. 3), and ii) the value of the reaction rate constant,  $k_{\text{obs.}}$ , is  $5.4 \times 10^{-4}$ . The  $k_{\text{obs.}t}$  values calculated from the data on the protonation kinetics of II at  $H_0 = -0.06$  and from the equation  $k_{\text{obs.}t} = f(H_0)$  show a good coincidence: they are 0.259 and 0.261, respectively ( $t = 8$  min).

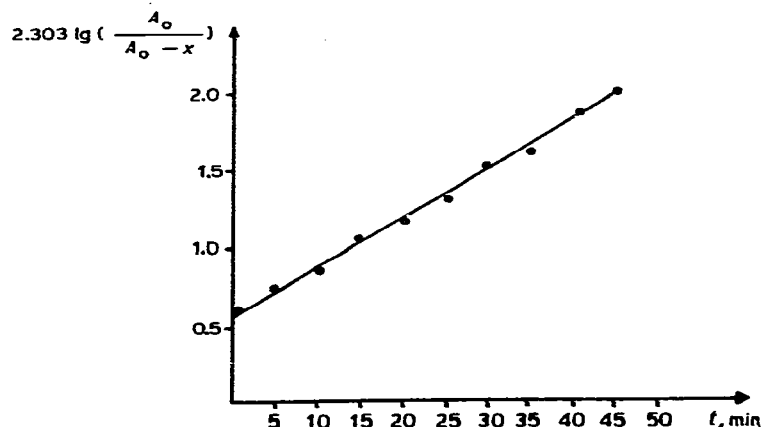


Fig. 3. Protonation kinetics of 6-dimethylaminofulvenmolybdenetricarbonyl (II) at  $H_0 = -0.06$ .  $y = 0.55 + 5.4 \times 10^{-4}t$ ;  $\Delta a = \pm 0.096$  at  $P = 0.95$ ,  $\pm 0.138$  at  $P = 0.99$ ;  $\Delta b = \pm 1.6 \times 10^{-5}$  at  $P = 0.95$ ,  $\pm 2.3 \times 10^{-5}$  at  $P = 0.99$ ;  $f = 9$ ;  $r = 0.999$ .

## Experimental

The IR spectra were run on a Zeiss-UR-20 spectrometer (LiF prism, cell thickness 0.11 mm). Duration of an experiment to measurement of  $k_{\text{obs}}$ .  $t = f(H_0)$  was 8 min.

The NMR spectra were recorded on a Bruker WH-180 spectrometer in trifluoroacetic acid (with  $\text{CDCl}_3$  as an external standard).

All solvents were purified and dried in argon atmosphere, solutions were prepared and cells and ampoules filled under argon.

The complexes I–III were obtained from 6-dimethylaminofulven and the corresponding acetonitrile complexes of metal carbonyls using a method given in ref. 6 and modified by us. The standard procedure to obtain 6-dimethylaminofulvenmolybdenetricarbonyl (II) is described below.

Acetonitrile complexes of metal carbonyls were obtained by the method described in ref. 7.

6-Dimethylaminofulven was obtained by the method described in ref. 8 from sodium cyclopentadienyl and dimethylamino-methoxycarboniummetosulphate.

### 6-Dimethylaminofulvenmolybdenetricarbonyl (II)

The acetonitrile complex of molybdenum carbonyl, obtained from 10.56 g (0.04 mol) of molybdenum hexacarbonyl in 320 ml acetonitrile, was dissolved with heating on a water bath, in 100 ml dried diglyme. To the solution obtained was added a solution of 4.8 g (0.04 mol) of 6-dimethylaminofulven in 100 ml dried diglyme. The reaction mixture was heated on a water bath at 60–70°C for 2 h and left to stand overnight at room temperature. Precipitated crystals were filtered off, washed with n-hexane, and dried under vacuum at 50–60°C (1 mm) for 6 h. 2.3 g of II was obtained. To the remaining solution was added 750 ml n-hexane and the mixture was left at overnight room temperature. Precipitated small crystals were filtered off, washed on the filter with n-hexane and dried under vacuum at 50–60°C (1 mm) for 6 h. 5.35 g of II was obtained. The total yield is 64%. The synthesis was conducted under an argon atmosphere. IR (KBr)  $\nu$ : 1920, 1800, 1624, 1450, 1420, 1410, 1365, 1345, 1287, 1250, 1170, 1133, 1060, 940, 800, 778, 657, 630, 615, 597, 507, 462  $\text{cm}^{-1}$ . PMR (acetone- $d_6$ )  $\delta$ : 3.46; 3.31 ppm ( $\text{CH}_3$ ), 5.73, 5.56 ppm (Cp–H), 8.10 ppm (C–H). Found: C, 43.63, 43.33; H, 3.49, 3.78; N, 4.84, 4.80; Mo, 31.85, 31.74%.  $\text{C}_{11}\text{H}_{11}\text{NMoO}_3$  calcd.: C, 43.87; H, 3.68; N, 4.65; Mo, 31.86%.

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