Contribution from the Istituto di Chimica Organica e Chimica Industriale dell'Università and Centro di Spettroscopia Molecolare del C.N.R., Viale Risorgimento 4, 40136 Bologna (Italy)

P.M.R. Spectra of Thiofene-Chromium-Tricarbonyl and of the Corresponding Monomethyl Derivatives

A. Mangini and F. Taddei

Received February 14, 1968

The P.M.R. spectra of thiophene-chromium-tricarbonyl and of the two monomethyl derivatives have been recorded both in chloroform-d₁ and acetone-d₆ solution. Analysis of the spectra, carried out with the aid of some deuterated compounds, shows that the $Cr(CO)_3$ group perturbs more strongly the α than the β protons of thiophene ring. Acetone solvent effect, which is greater for the complex than for the free ligand, affects the α protons more than the others.

Introduction

Thiophene-chromium-tricarbonyl was first prepared by Fischer.[1] Physical and structural characteristics[1,2] of this compound are in general similar to those of benzene-chromium-tricarbonyl. In this compound the chromium atom can in fact be considered to be bonded to the π electron cloud of the thiophene molecule.[1]

We have devoted our interest to the study of the perturbation exerted by the $Cr(CO)_3$ group on the π electron cloud of the thiophene ring. The results of a P.M.R. investigation on thiophene-chromium-tricarbonyl and its monomethyl derivatives are here reported. The spectra of the complexes and of the corresponding free ligands, analyzed for the sake of comparison, were recorded both in chloroform-d_1 and acetone-d_6 to test the presence and the magnitude of solvent-solute interactions in this system.

Experimental Section

Thiophene-chromium-tricarbonyls were prepared by exchange reactions from benzene-chromium-tricarbonyl and oxigen-free thiophene (or mono-methyl thiophene): the latter compounds were always used in a large excess. The reaction was carried out in a sealed glass tube, containing a dry-nitrogen atmosphere, at 160-170°C for 3-4 hours. The thiophene complexes were separated from benzene-chromium-tricarbonyl unreacted by chromatography (standard alumina), and sublimed under vacuum (90°C, 0.6 mmHg). Orange-red crystals were obtained; yield $\sim 3\%$ with respect to benzene-chromium-tricarbonyl, which was recovered almost quantitatively. Melting points could not be obtained since thiophene-chromium-tricarbonyls are asily decomposed. Analysis: thiophene-chromium-tricarbonyl, $C_7H_4CrO_3S$, requires $C\% = 38.16$, $H\% = 1.83$, found $C\% = 38.51$, $H\% = 1.92$; 2-methyl thiophene-chromium-tricarbonyl, $C_8H_6CrO_3S$ requires $C\% = 41.00$, $H\% = 2.58$, found $C\% = 41.13$, $H\% = 2.47$; 3-methyl thiophene-chromium-tricarbonyl, $C_8H_6CrO_3S$, requires $C\% = 41.00$, $H\% = 2.58$, found $C\% = 41.16$, $H\% = 2.56$. Deuterated thiophenes were prepared by known methods:[3] isotopic purity was checked by P.M.R. analysis.

P.M.R. spectra were obtained on a Varian DP 60 spectrometer operating at 56.4 Mc/s. Both the spectra of the free ligands and of thiophene complexes were recorded in chloroform-d_1 and acetone-d_6: the concentration was about 0.5 *M* and 0.2 *M* respectively for the former and the latter compounds. Decomposition occurs especially in acetone solution and spectra have to be recorded immediately after the solutions have been prepared.

Results and Discussion

The P.M.R. spectrum of thiophene and of the corresponding chromium-tricarbonyl derivative is reported in Figure 1.

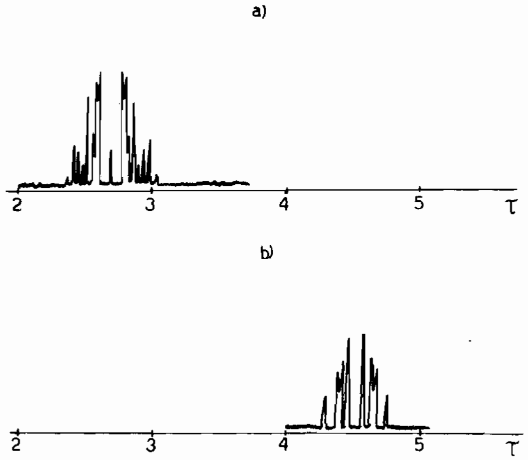

Figure 1. P.M.R. spectrum of thiophene (a) and thiophene-chromium-tricarbonyl (b) in $CDCl_3$ solution.

---

[1] E. O. Fischer, K. Öfele, *Chem. Ber.*, *91*, 2395 (1958).
[2] M. F. Bailey, L. F. Dahl, *Inorg. Chem.*, *4*, 1306 (1965).
[3] R. A. Hoffman, *Arkiv for Kemi*, *8*, 29 (1956).

Table I. Chemical shifts in τ units for deuterated thiophenes and for the corresponding chromium-tricarbonyl complexes measured in $CDCl_3$ solution (values in parentheses refer to acetone solution)

Compound	τ(3)	τ(4)	τ(5)
2,5-dideutero-thiophene	2.90 (2.85)	2.90 (2.85)	—
3,5-dideutero-2-methyl-thiophene	—	3.11 (3.11)	—
2-deutero-3-methyl-thiophene	—	3.07 (3.06)	2.78 (2.69)
(2,5-dideutero-thiophene)$Cr(CO)_3$	4.41	4.41	—
(3,5-dideutero-2-methyl-thiophene)$Cr(CO)_3$	—	4.47	—
(2-deutero-3-methyl-thiophene)$Cr(CO)_3$	—	4.44	4.60

Table II. Chemical shifts (τ units) and coupling constants (c/s) for thiophene, thiophene-chromium-tricarbonyl and their monomethyl derivatives measured in $CDCl_3$ solution

Compound	τ(2)	τ(3)	τ(4)	τ(5)	$\tau(CH_3)$	$J_{4,5}(J_{2,3})$	$J_{3,5}(J_{2,4})$	$J_{2,5}$	$J_{3,4}$
Thiophene	2.65	2.86	2.86	2.65	—	5.0	0. 9	3.0	4.1
2-methyl-thiophene	—	3.21	3.09	2.92	7.54	5.3	1.4	—	3.4
3-methyl-thiophene	3.09	—	3.09	2.78	7.73	4.8	1.2	3.4	—
(thiophene)$Cr(CO)_3$	4.63	4.39	4.39	4.63	—	2.8	1.2	0.9	2.2
(2-methyl-thiophene)$Cr(CO)_3$	—	4.64	4.47	4.78	7.72	3.4	—	—	2.1
(3-methyl-thiophene)$Cr(CO)_3$	4.88	—	4.44	4.60	7.73	3.8	—	—	—

Table III. Chemical shifts (τ units) and coupling constants (c/s) for thiophene, thiophene-chromium-tricarbonyl and their monomethyl derivatives measured in acetone-d_6 solution

Compound	τ(2)	τ(3)	τ(4)	τ(5)	$\tau(CH_3)$	$J_{4,5}(J_{2,3})$	$J_{3,5}(J_{2,4})$	$J_{2,5}$	$J_{3,4}$
Thiophene	2.54	2.86	2.86	2.54	—	4.6	1.1	3.6	2.8
2-methyl-thiophene	—	3.20	3.09	2.84	7.55	4.8	1.2	—	3.1
3-methyl-thiophene	2.99	—	3.07	2.69	7.76	4.8	0.9	3.1	—
(thiophene)$Cr(CO)_3$	4.07	4.07	4.07	4.07	—	—	—	—	—
(2-methyl-thiophene)$Cr(CO)_3$ [a]	—	4.24	4.24	4.24	7.70	—	—	—	—
(3-methyl-thiophene)$Cr(CO)_3$ [a]	4.24	—	4.24	4.08	7.68	—	—	—	—

[a] Spectra very poorly resolved.

In acetone solution the P.M.R. spectrum of the complex displays a singlet at 4.07 τ. The assignment of the chemical shifts to α and β protons in thiophene has been done.[4] For thiophene-chromium-tricarbonyl, in chloroform-d_1 solution, since the resonance of ring protons is shifted to higher field relatively to the free ligand, the assignment of spectral frequencies, must be checked.* For this purpose some deuterated compounds were prepared: the corresponding chemical shifts are reported in Table I. For the complexes only the spectra in $CDCl_3$ solution were recorded, since thiophene-chromium-tricarbonyl in acetone solution displays a single line and the assignment in the latter solvent is straightforward. In Tables II and III proton chemical shifts and J_{HH} coupling constants for the complexes and the corresponding free-ligands are reported.

These results show that for thiophene-chromium-tricarbonyl the resonance of α protons in $CDCl_3$ solution is found at higher field than that of β protons: this situation is thus opposite to that found for thiophene in the same solvent. This applies also to the monomethyl derivatives.

A few comments can be deserved to these results.

First of all it is found that the $Cr(CO)_3$ group does not perturb the thiophene ring simmetrically as it is seen for benzene-chromium-tricarbonyl.[7,8] The difference between the proton chemical shift in the free ligand and that in the complex shows that the α protons display a higher diamagnetic shift than the corresponding β protons ($\delta\alpha = 1.98$ p.p.m., $\delta\beta = 1.53$ p.p.m. in $CDCl_3$, $\delta\alpha = 1.53$ p.p.m., $\delta\beta = 1.21$ p.p.m. in acetone-d_6, to be compared with 2.04 and 1.72 p.p.m. for the benzene derivative[8] in CCl_4 and acetone respectively).

A quite similar differentiation is found for the solvent effect: the α protons in the complexed thiophenes are those more perturbed in acetone solution. This solvent effect is probably due to the formation of hydrogen-bonding with the C=O group of this solvent. For thiophene itself α and β protons are differently affected by solvent, as can be observed by comparing the results reported in Tables II and III (α protons more shifted to lower field) but the low field shift found is significantly smaller than for the carbonyl complexes.

On the other hand these results are not in complete agreement with X-ray structural analysis of this compound.[2] It is difficult at present to evaluate the entity of charge density differences between α and β position from P.M.R. results and eventually to estimate if differences of this kind can provide changes in bond distances which could be shown by X-ray analysis.

(*) The analysis of AA'BB'[5] (unsubstituted terms) and ABC[5] (monomethyl derivatives) groups was performed with the aid of the LAOCOON II program,[6] using an IBM 7094 computer.

(4) R. A. Hoffman, S. Gronowitz, *Arkiv for Kemi, 16* 515 (1960) .

(5) J. A. Pople, W. G. Schneider, H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw Hill Company, New York (1959).

(6) Program kindly supplied by Dr. S. Castellno, Mellon Institute, Pennsylvania.

(7) W. McFarlane, S. O. Grim, *J. Organometall. Chem.*, 5, 147 (1966).

(8) A. Mangini, F. Taddei, *Inorg. Chim. Acta,* this volume.

Also the J_{HH} coupling constants show a behaviour similar to that observed for benzene-chromium-tricarbonyls.[8,9,10] These constants are in fact 1-2c/s lower in the complex than in the free ligand. As pointed out previously[9] for benzene derivatives no evidence is provided by these constants for π electron localization: probably the lowering of their values could be ascribed to the electronegativity of the $Cr(CO)_3$ group.

The P.M.R. spectra of thiophene-chromium-tricarbonyl show thus that the influence of complex formation is strong both on α and β protonts. This is in agreement with previous suggestions[1] that the thiophene ring should be bonded to the metal atom with the π electron cloud.

On the other hand the stronger perturbation observed for α protons in thiophene-chromium-tricarbonyl, both higher diamagnetic shift due to complex formation and solvent effect, could be probably ascribed to a stronger bonding of the chromium atom with the region of the thiophene ring nearest to the sulphur atom. Again this point is not confirmed by X-ray analysis,[2] but the same arguments provided above can be put forward. M.O. calculations of charge densities in this complex should perhaps be useful to provide an answer to this problem.

(9) Z. Buczkowsky, *Boll. Acad. Polon. des Sciences*, *13*, 531 (1965).
(10) H. P. Fritz, C. G. Kreiter, *J. Organometall. Chem.*, *7*, 427 (1967).