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Chemical shift anisotropy of carbon-13 nuclei in carbonyl groups of (η^4-norbornadiene)tetracarbonylchromium and metal VIb hexacarbonyls

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Abstract

The longitudinal nuclear spin relaxation times and NOE enhancement factors of ^{13}C nuclei of the compounds named in the title, dissolved in $CDCl_3$, were measured in two magnetic fields. The results are interpreted in terms of ^1H–^{13}C dipole–dipole relaxation and ^{13}C chemical shift anisotropy relaxation caused by rotational diffusion. Data on shielding tensors of the ^{13}C nuclei in the terminal metal bonded carbonyl groups are reviewed.

Introduction

Investigation of the longitudinal nuclear magnetic relaxation of ^{13}C spins provides valuable information on inter- and intramolecular dynamics in liquids. It has been shown that the chemical shift anisotropy mechanism (CSA) dominates in the relaxation of the carbonyl ^{13}C nuclei in moderate and strong fields [1–3]. This opens new possibilities for the investigation of dynamics in carbonyl-metal complexes, provided that a convenient method for the estimation of the shielding anisotropy, $\Delta\sigma$, is available. Such a method has been proposed by Brownlee et al. [1]. Assuming axial symmetry of the shielding tensor of the ^{13}C nucleus in the terminal CO group, the $\Delta\sigma$ parameter is calculated from the equation:

$$\Delta\sigma = 1.5(\delta - \delta_{\parallel}) \qquad (1)$$

The chemical shift δ is easily obtainable from the high resolution NMR spectrum. The $\delta_{\parallel}$ parameter can be assumed, following Mahnke et al. [2], to be equal to that for carbon monoxide. The validity of this method of evaluation of $\delta_{\parallel}$ was supported by results obtained for $Fe(CO)_5$ and $Ni(CO)_4$ in solutions. Further experimental data for a number of transition metal carbonyls in the solid state are now available [4–7]. In this work $\Delta\sigma$ and $\delta_{\parallel}$ parameters for (η^4-norbornadiene)tetracarbonylchromium (NBDCr) and for Group VIb metal hexacarbonyls in $CDCl_3$ solutions have been determined on the basis of the measurements of longitudinal relaxation times. Literature data concerning the shielding tensors of the terminal carbonyl carbons have also been collated.

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Experimental

(η^4-Norbornadiene)tetracarbonylchromium was prepared by the standard method [8]. Group VIb metal hexacarbonyls (purchased from Merck) were sublimed in vacuum before use. A solution of NBDCr (0.1 *M*) and solutions of $Cr(CO)_6$ (0.1 *M*), $Mo(CO)_6$ (0.1 *M*) and $W(CO)_6$ (0.1 *M*) were prepared under an argon atmosphere, filtered through silica gel and sealed in 5 mm NMR tubes under vacuum. Measurements were carried out at 303 K and standard recording conditions using a Bruker AM-500 spectrometer operating at 11.7 T and Bruker 360 spectrometer operating a 8.4 T.

The experimental procedures for NOE measurement and for T_1 (saturation–recovery) determination have been described in detail [3]. The results in Tables 1 and 2 represent the mean values of 3 to 6 determinations. The accuracy estimated on the basis of the measurement reproducibility and of calculated standard errors is 5% for relaxation times and ± 0.1 for η values.

Results and discussion

The NOE enhancement factors, η, for protonated carbons of NBDCr and longitudinal relaxation times, T_1, of ^{13}C nuclei were measured in two magnetic fields, 8.4 and 11.7 T. Results are presented in Tables 1 and 2.

Inspection of Table 1 shows that the relaxation times for protonated ^{13}C nuclei of NBDCr are independent of field strength and their η coefficients are close to the

Table 1

Relaxation data for protonated carbons of (η^4-norbornadiene)tetracarbonylchromium

Carbon	$B_0 = 8.4$ (T)		$B_0 = 11.7$ (T)		$T_{1,DD}$ (s)
	T_1 (s)	η	T_1 (s)	η	
1, 4	4.67	2.05	4.77	1.94	4.80
2, 3, 5, 6	4.43	2.00	4.44	1.75	4.80
7	2.57	1.95	2.71	1.83	2.84

Table 2

Relaxation data, correlation times and chemical shift anisotropies for carbonyl carbons in (η^4-norbornadiene)tetracarbonylchromium and Group VIb metalhexacarbonyls

Compound	T_1 (s) $B_{0,1} = 8.4$ (T)	T_1 (s) $B_{0,2} = 11.7$ (T)	$(\frac{B_{0,1}}{B_{0,2}})^2 \cdot T_1(B_{0,1})$	τ_c (ps)	$\Delta\sigma$ (ppm)
$NBD \cdot Cr(CO)_4$ (CO-*trans*)	10.6	6.26	5.46	10.3 [a]	431
$NBD \cdot Cr(CO)_4$ (CO-*cis*)	11.8	6.40	6.08	10.3 [a]	427
$Cr(CO)_6$	12.4	6.51	6.39	9.5	442
$Mo(CO)_6$	12.1	6.68	6.24	10.8	412
$W(CO)_6$	12.4	6.01	6.39	10.6	429

[a] Value calculated assuming anisotropic rotational diffusion of (η^4-norbornadiene) tetracarbonylchromium.

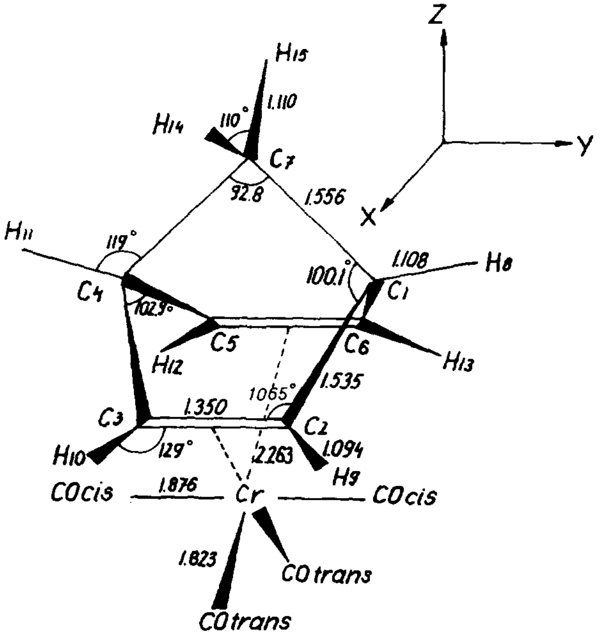

Fig. 1. Assumed molecular structure of (η^4-norbornadiene)tetracarbonylchromium. The dihedral angle $C_1C_2C_3H_{10}$ is 184° [10] (angles are in degrees and bond lengths in Å).

maximum value, 2.0. Thus, the ^1H–^{13}C dipole–dipole relaxation mechanism is the dominant one for those carbons [9,10]. Moreover, it indicates that molecular tumbling is fast enough to ensure the extreme narrowing condition [9,10]. As a matter of fact the $\omega_0\tau_c$ value is smaller than 0.01 (see below). Using the formula [9]:

$$T_{1,DD} = (\eta_{max}/\eta) \cdot T_1 \tag{2}$$

the dipole–dipole relaxation times, $T_{1,DD}$, were calculated and were used as a source of information about the rate of molecular reorientation.

Since the dipole–dipole interaction energy is inversely proportional to the sixth power of the distance between the interacting spins, precise knowledge of the lengths of the C–H bonds is important. Unfortunately, there are no such data for the NBDCr molecule in the literature. Therefore the bond lenghts used in our calculations were those reported for free norbornadiene determined by the electron diffraction method and verified by NMR measurements in the oriented phase [10]. The C–H bond length of free benzene [13] and that of its tricarbonylchromium complex [14] differ by 0.5% and with this as an analogy it was decided to increase the olefinic C–H bond length in NBDCr as compared to free norbornadiene by the same proportion. The lengths of all the C–H bonds used in calculations were increased by 1.5% to take into account the ground state vibrations [15].

The interactions between the ^{13}C and ^1H nuclei, which were not directly bonded, made only a minor contribution to the relaxation, but this was not negligible. To include them in numerical calculations one must assume a structure for the investigated molecule. The structure illustrated (Fig. 1) was deduced from those of norbornadiene [12] and its (triphenylphosphino)tricarbonylchromium complex [16]. The tumbling of the NBDCr molecule has been described in terms of the theory of

Table 3

Illustration of the influence of T_1 and of the type of rotational diffusion model, upon rotational diffusion coefficients

Rotational diffusion model	Carbon position						D_x [e]	D_y [e]	D_z [e]	$1/3\mathrm{Tr}(D)$ [e]
	1, 4		2, 3, 5, 6		7					
	T_1 (s)	ΔT_1 [c] (s)	T_1 (s)	ΔT_1 [c] (s)	T_1 (s)	ΔT_1 [c] (s)				
Spherical top [a]	4.80	−0.38	4.80	−0.07	2.84	0.14	1.62	1.62	1.62	1.62
Symmetrical top [a]	4.80	0.03	4.80	−0.32	2.84	0.04	0.42	0.42	5.72	2.19
		0.01		−0.07		0.01	2.42	2.42	0.64	1.83
Assymmetrical top [a]	4.80	0.00	4.80	0.00	2.84	0.00	0.57	1.23	3.36	1.72
		0.00		0.00		0.00	0.94	1.62	2.29	1.62
Asymmetrical top [b]	4.56	0.00	5.04	0.00	2.70	0.00	0.45	0.25	6.02	2.24
Asymmetrical top [b,d]	4.56	0.05	4.56	−0.18	2.98	0.01	0.49	1.52	3.07	1.69

[a] The experimental values of T_1 were assumed in calculation. [b] T_1 values changed by 5% relative to experimental values. [c] $\Delta T_1 = T_1 - T_{1,\mathrm{calc}}$ where $T_{1,\mathrm{calc}}$ is the relaxation time calculated from D values. [d] Least squares solution only. [e] Values $\times 10^{10}$ (s^{-1}).

rotational diffusion [17]. The experimental relaxation times $T_{1,\mathrm{DD}}$ from Table 1 can be reproduced with acceptable accuracy even within the rotational diffusion model of a spherical top (Table 3). The molecule is not, however, perfectly spherical and three rotational diffusion coefficients are necessary to describe its reorientation. It must however, be realized that there are only three sets of relaxation data available. We have found numerically two solutions of the problem and both appear to be reasonable (Table 3). We attempted to predict how far these solutions are affected by the precision of the experimental data by recalculating, changing the $T_{1,\mathrm{DD}}$ values from Table 1 by $\pm 5\%$. Another calculation, assuming the symmetrical top diffusion [15] model, was performed too. For some sets of relaxation times we got one or two reasonable solutions, for some others the system of equations had only the least square solution (Table 3). These alternative calculations yield diffusion coefficients which may differ by as much as a factor of four. The mean values of the rotational diffusion coefficient $(D_x + D_y + D_z)/3$ are not so divergent. The above calculations show that the rotation about the molecular z axis is the fastest one, which is to be predicted from the shape of the molecule. Only in one case in which cylindrical symmetry was assumed did one of the two solutions contradict this conclusion.

In Table 2 it is seen that the relaxation times for carbonyl carbons are proportional to the square of the magnetic field strength (see column 2 in Table 2). This proves the CSA relaxation mechanism to be the only important one in this case [9,10]. This conclusion is in agreement with previous observations made on similar compounds [3]. This allows us to estimate the chemical shift anisotropy parameters for carbonyl carbons using the calculated rotational diffusion coefficients. In general the CSA relaxation rate is proportional to the expression $(1 + \zeta^2/3)(\Delta\sigma)^2$ where the asymmetry parameter [10] $\zeta = (\sigma_{xx} - \sigma_{yy})/\sigma_{zz}$. In the case under discussion one can, however, make the reasonable assumption of axial symmetry of the shielding tensor that is involved [2,3,6,7]. In the case of metal hexacarbonyls, this property is a consequence of the molecular symmetry. Thus, in order to calculate $\Delta\sigma$ ($\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$) we may use the simplified equation [9,17]:

$$1/T_{1,\mathrm{CSA}} = (2/15)\omega_0^2(\Delta\sigma)^2\tau_c \qquad (3)$$

where τ_c is rotational correlation time of the symmetry axis of the shielding tensor. In the case of the NBDCr molecule, the correlation time can be calculated from rotational diffusion coefficients for isotropic as well as for anisotropic reorientations [10,17]. For both cases, the results are not very different. So, in view of the doubts expressed above concerning the reliability of the anisotropic rotational diffusion coefficients, we prefer the value based on the assumption of isotropic reorientation. The rotational correlation times for the spherical molecules of metal hexacarbonyls were evaluated using the value of τ_c determined for NBDCr and assuming that correlation times is proportional to molecular volume [18–20]. Values of $\Delta\sigma$ calculated from eq. 3 are collected in Table 2. In view of the many simplifying

Table 4

Experimental shielding data for carbon nuclei in terminal metal bonded carbonyl groups

Kind of carbonyl group	δ (ppm)	$\Delta\sigma$ (ppm)	$\delta_{\parallel}$ (ppm)	$\delta_{\perp}$ (ppm)	Method [b]	Ref.
CO	181	406	-90 ± 20	316	PP	6,21,22
$C_6H_5N \cdot Cr(CO)_5$	221	501	-113 ± 40	388	T_1	3
$NBD \cdot Cr(CO)_4$ (CO-*trans*)	229	431	-58 ± 30	373	T_1	[a]
$NBD \cdot Cr(CO)_4$ (CO-*cis*)	226	427	-59 ± 30	368	T_1	[a]
$Cr(CO)_6$	211	442	-83 ± 30	359	T_1	[a]
	212	423	-70 ± 15	353	PP	6
$MO(CO)_6$	201	412	-74 ± 30	338	T_1	[a]
	202	417	-75 ± 15	343	PP	6
$W(CO)_6$	191	429	-95 ± 30	334	T_1	[a]
	192	395	-71 ± 15	324	PP	6
$Fe(CO)_5$	212	425	-71 ± 15	354	T_1 + Th, PP	2,4
$(\eta^5\text{-}C_5H_5)_2Fe(CO)_4$ terminal	211	444	-85 ± 15	354	PP	6
$Ni(CO)_4$	193	395	-70 ± 15	325	T_1 + Th, PP	2,4
$Ru_3(CO)_{12}$ axial	210	396	-54 ± 10	342 [c]	SS	7
equatorial	189	395	-74 ± 10	321 [c]	SS	7
$Rh_6(CO)_{16}$ terminal	181	386	-76 ± 10	310 [c]	SS	7
$Rh_2(CO)_4Cl_2$	180	402	-99	303 [c]	PP	5,6
$Os_3(CO)_{12}$ axial	186	367	-59 ± 10	309 [c]	SS	7
equatorial	171	353	-64 ± 10	289	SS	7
$Ir_4(CO)_{12}$	156	355	-81 ± 10	274	SS	7

[a] This work. [b] T_1-measurements of longitudinal nuclear spin relaxation times due to chemical shift anisotropy mechanism; Th-theoretical calculations PP-NMR powder pattern; SS-spinning sideband technics. [c] Mean value of two shielding components.

assumptions that have been made, it is very difficult to estimate the accuracy of the determined $\Delta\sigma$ parameters, but we believe them to be around 10%.

The literature data on shielding tensors of carbons in metal bonded carbonyl groups, together with those obtained in this work are collated in Table 4. The shielding parameters that we obtained for Group VIb metalhexacarbonyls are in good agreement with those which Gleeson and Vaughan [6] measured by solid state NMR of polycrystalline samples. The shielding anisotropies of terminal carbonyl carbons (Table 4) are large (350–500 ppm) and seem to depend on the metal. At the same time the shielding tensor component parallel to the CO bond direction, $\delta_{\parallel}$ falls within a relatively narrow range (-54 to -113 ppm). Taking into account the accuracy of determination of that parameter, the actual range may be even narrower. The substitution of $\delta_{\parallel} = -74$ ppm into eq. 1 leads to the empirical formula:

$$\Delta\sigma = 1.5\delta + 111 \qquad (4)$$

which should not bias the estimated parameter by more than 10%. Such an accuracy is often acceptable in investigations of molecular dynamics by nuclear spin relaxation methods. On the other hand one cannot exclude the possibility of some differences between $\delta_{\parallel}$ values for the terminal carbonyl carbons in the different molecular sites. To detect such effects one must, however, apply a more accurate determination procedure than that used in this work. Probably the method based on chemical shift determination in the oriented phase would be the most appropriate [23], and this approach is now being attempted.

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