Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE MÖSSBAUER EFFECT IN NITROSOAROMATIC IRON TRICARBONYLS

E. FRANK* AND D. ST. P. BUNBURY
Department of Physics, Manchester University, (Great Britain)

(Received February 2nd, 1970)

SUMMARY

We report in this paper Mössbauer effect data on five nitrosoaromatic iron tricarbonyls with different substituents attached to the phenyl group. These data show that the structure is the same in all the cases and not, as has previously been suggested, a function of the substituents. Very recent X-ray work on one of these compounds has established the structure as dimeric and so all of them must be considered to have this configuration.

INTRODUCTION

Some time ago Koerner von Gustorf and co-workers reported[1] the photo- and radiochemical reduction of mixtures of aromatic nitrocompounds and $Fe(CO)_5$. They suggested, on the evidence of IR, UV, melting point and molecular weight data that the $[R_1R_2C_6H_3NOFe(CO)_3]_n$ compounds obtained (where either $R_1 = H$ and $R_2 = H$, 4-$COOCH_3$, 2-(2′-$NO_2C_6H_4$) or Cl or CH_3 in 2-, 3- or 4-positions, or else $R_1 =$ 2-CH_3 and $R_2 =$ 3-Cl) were monomeric or dimeric depending on the substituents attached on the benzene nucleus. Furthermore they proposed that the structure of the monomeric unit consists essentially of distorted tetragonal pyramids, where three of the coordination positions were occupied by carbonyl groups and the fourth an fifth positions by the nitrogen and oxygen atoms of the nitroso group. On the other hand the dimeric structure would arise through the interaction of two of those units, which would be bridged by two nitroso groups. Each iron atom thus would be bonded to one nitrogen and one oxygen atom of the bridging groups.

Recently it has been shown[2,4] that in the carbonyl-bridged compounds $[(CO)_3Fe(COC_6H_5)]_2$ and $(CO)_2RFe(COC_6H_5)_2Fe(CO)_3$ [where $R = N(C_2H_5)_2$ and NC_5H_{10}] the bridging is such that both carbon atoms of the bridging groups are attached to the same iron atom. Such a structure was also conceivable in the case of the nitrosoaromatic iron tricarbonyls but very recent X-ray work[5] on the 2-CH_3, 3-Cl derivative, has shown that the structure is in fact as depicted in Fig. 1.

---

* Research fellow from the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina. Present address: Gerencia de Investigaciones, CNEA, Avda Libertador 8250, Buenos Aires, Argentina.

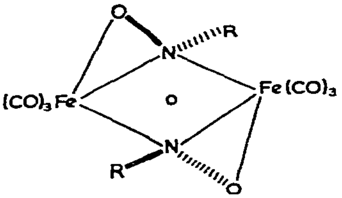

Fig. 1. Established structure of $[2\text{-}CH_3, 3\text{-}ClC_6H_3NOFe(CO)_3]_2$ (see ref. 5) ($R = 2\text{-}CH_3, 3\text{-}ClC_6H_3$).

In the last few years Mössbauer spectroscopy has been widely used for solving structural problems in chemistry[6,7]. The information which can be obtained is related to coordination numbers, symmetry, oxidation states and types of bonding. In practice it is rarely possible to isolate effects due to changes in symmetry and in types of bonding as variations in both of these influence the Mössbauer parameters.

We felt at the beginning of the present research, when the results of the X-ray work[5] were not yet known, that the Mössbauer effect would provide valuable information concerning the coordination in these compounds and we therefore chose five samples which should be representative of the different types of behaviour: (*i*) the anisole derivative which was claimed to be monomeric; (*ii*) the $2\text{-}CH_3$, 3-Cl derivative and two forms of benzene derivatives obtained under different experimental conditions, which should be dimeric; and (*iii*) the *p*-toluene derivative which Koerner von Gustorf and co-workers[1] claim to be a mixture of both forms. We expected a noticeable change in quadrupole splitting when passing from a monomeric to a dimeric structure, due to the fact that in this last type of structure the constraints imposed on the N–Fe and O–Fe bonds are intuitively much smaller than in the case of the proposed monomeric structure. The change in geometry would involve distinct contributions from the various iron *d* orbitals and thus a change in quadrupole splitting would arise. At the same time we would expect a change in Debye–Waller factor with such a change of structure due to the fact that we are dealing with molecular crystals, where the vibrational modes are a property rather of the molecule than of the crystals themselves. When passing from one structure to another, different low energy vibrational modes are effective, which could affect the Debye–Waller factor which is a function of the frequency spectrum. It must be remembered that in this type of crystal, optical modes may lie below the accoustic ones in contrast to simple solids.

These ideas have not been exhaustively tested yet, but several systems have been examined which suggest that such changes can reasonably be expected. For example, Sano *et al.*[8] found that in bis(pyridine)cobalt(II) dichloride, used as a ^{57}Fe Mössbauer source at 80° K, when passing from a monomer to a polymer there is a large change in *f* factors (from 0.3 to 0.53), isomer shifts (1.03 to 1.35 mm/sec *vs.* a 310 stainless steel absorber) and in quadrupole splittings (from 3.14 to 1.13 mm/sec). These changes are larger than we would expect in our case because the polymerization involves the change from a tetrahedral to an octahedral structure, which represents a much larger structural rearrangement than the dimerization which is postulated in ref. 1 for the compounds under discussion. Similarly, a change in *IS* and *QS* has been observed by Aleksandrov *et al.*[9] when passing from $(n\text{-}C_4H_9)_2Sn(OCOCCH_2CH_3)_{4-n}$ $(n = 1,2,3)$ to their polymers. For these compounds the change in *IS* of 0.05 mm/sec and of 20 % in *QS*, from around 3.10 to 3.70 mm/sec is typical.

Wertheim and Herber[10] report a change of 0.09 mm/sec in the *QS* and of

0.05 mm/sec in the *IS* when passing from (COT)Fe$(CO)_3$ to (COT)$Fe_2(CO)_6$ (where COT = cyclooctatetraene) which involves practically no distortion in comparison to the change proposed by Koerner von Gustorf and co-workers. Finally, a change in *IS* of 0.06 mm/sec and of 0.07 mm/sec in *QS* has been observed when passing from Fe(salen)Cl to $[Fe(salen)Cl]_2$ (where salen is the Schiff base of salicylaldehyde and ethylenediamine)[11].

RESULTS AND DISCUSSIONS

The Mössbauer spectra were taken using a conventional spectrometer. A 20th Century Electronics Xe-filled proportional counter with exit window and fitted with concentric shields of copper, tin and lead was used. To allow comparisons of absorption intensities and hence of recoilless fractions at different temperatures and among different samples, the geometry was kept constant and before and after each run the output of the single channel analyzer was checked. Correction for background due to unwanted types of radiation was not performed because the single channel analyzer output remained practically constant over the whole series of measurements and the amount had been estimated to be around 20%, using the conventional techniques of extrapolation of a smooth curve and folding of the photopeak of detected gamma rays with a Gaussian profile[12].

A weighed amount of sample, of the order of 20 mg/cm^2 (that is ca. 8×10^{-2} mg ^{57}Fe/cm^2), was pressed between two perspex discs, covering a known area. All the five samples were first measured at room and liquid nitrogen temperatures and then, in a second set of runs, at room, liquid nitrogen and several intermediate temperatures. Complete reproducibility, within experimental error, was achieved. In all cases we have found a two-peak spectrum with slightly different intensity ratios. A typical example is shown in Fig. 2. The relevant quadrupole splitting and isomer shift data

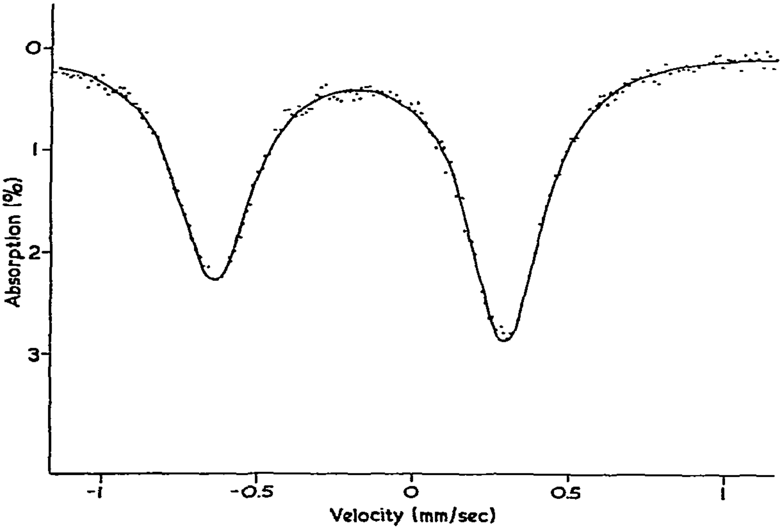

Fig. 2. Mössbauer spectrum at room temperature of 2-methyl-3-chloronitrosobenzene iron tricarbonyl, referred to the ^{57}Co in Pd source used.

at room and liquid nitrogen temperatures are shown, together with the widths at half height in Table 1. The errors correspond to the r.m.s. deviation of each of the parameters. The isomer shift data are referred to a sodium nitroprusside standard. Fig. 3 shows the typical temperature dependence of quadrupole splitting and isomer shift. The case shown corresponds to one of the benzene derivatives, labelled as (I) in Table 1.

The two-peak spectra do not exclude immediately structures of the type found for the carbonyl bridged compounds[2,4], because of the possibility of superimposing two one-peak spectra. Nevertheless even without considering the results of the X-ray study[5] such a possibility could be excluded on the basis of the following arguments:

TABLE 1

MÖSSBAUER DATA FOR NITROSOAROMATIC IRON TRICARBONYLS $[R_1R_2C_6H_3NOFe(CO)_3]_2$ AT ROOM AND LIQUID NITROGEN TEMPERATURES

R_1	R_2	Temp.	Quadrupole splitting (mm/sec)	Isomer shift (mm/sec)	Width 1[a] (mm/sec)	Width 2[a] (mm/sec)
p-OCH_3	H	Room	0.952±0.008	0.255±0.005	0.274±0.009	0.302±0.010
		liq. N_2	0.960±0.010	0.212±0.006	0.265±0.008	0.284±0.008
p-CH_3	H	Room	0.943±0.008	0.263±0.005	0.294±0.015	0.295±0.014
		liq. N_2	0.955±0.008	0.226±0.005	0.297±0.006	0.301±0.005
o-CH_3	m-Cl	Room	0.919±0.009	0.264±0.005	0.272±0.010	0.291±0.010
		liq. N_2	0.920±0.007	0.233±0.005	0.310±0.015	0.315±0.015
H(I)[b]	H(I)[b]	Room	0.950±0.009	0.250±0.005	0.285±0.008	0.298±0.008
		liq. N_2	0.959±0.007	0.211±0.005	0.300±0.007	0.299±0.008
H(II)[b]	H(II)[b]	Room	0.967±0.010	0.257±0.006	0.299±0.010	0.303±0.010
		liq. N_2	0.970±0.008	0.216±0.004	0.295±0.010	0.300±0.010

[a] 1 and 2 refer respectively to the peak at lower and higher velocity. [b] (I) and (II) produced under different experimental conditions, *i.e.* with and without stirring during the reduction.

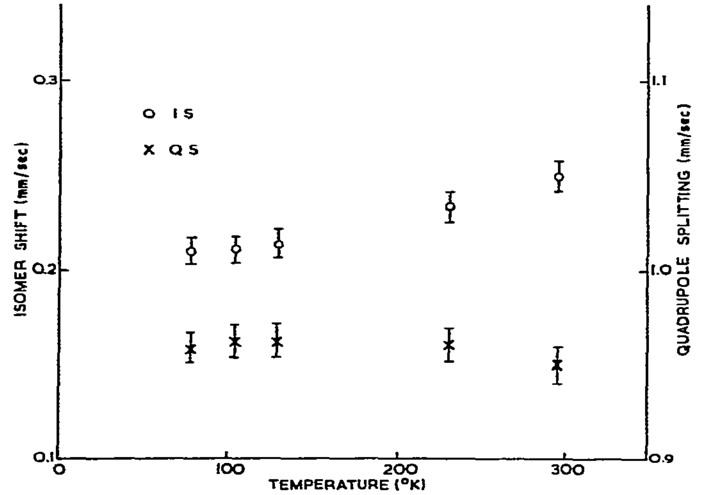

Fig. 3. Isomer shift (o) and quadrupole splitting (×) as a function of temperature for a sample of $[C_6H_5NOFe(CO)_3]_2$

(*i*) the existence of such a structure implies the existence of two different iron atoms with five nearest neighbours, three of them carbon atoms and the other two either two nitrogen or two oxygen atoms. In each case there is a large enough lowering of the symmetry from cubic to lead to a quadrupole-split spectrum; (*ii*) if the peaks correspond to two different sites, one of them would have far too negative an isomer shift, of the order of – 0.20 mm/sec (*vs.* sodium nitroprusside), which is not consistent with the available data in the literature[6,13] for similar compounds. On the other hand we ruled out the possiblity of superposition of two two-peak spectra with similar parameters, due to the fact that in all cases we get good fits with line widths which are close to 0.300 mm/sec which is only 0.050 mm/sec worse than the line width we obtain for sodium nitroprusside. It is for these reasons that we concluded that we were dealing in all cases with only one quadrupole split spectrum, that is there exists only one unique configuration of nearest neighbours around the iron atom, and therefore, asymmetric structures had to be discarded from the beginning.

Isomer shifts

As can be seen from Table 1 the values of isomer shift lay, at liquid nitrogen temperature, in a range of less than 0.025 mm/sec, around 0.22 mm/sec *vs.* sodium nitroprusside. These are reasonable values for iron carbonyls as can be seen from Table 4.8 of ref. 6, and they are consistent with the zero oxidation state of the iron atom. The variation in isomer shift with temperature is of the order of 0.06 mm/sec when passing from room to liquid nitrogen temperature. This value can be interpreted as due to second order Doppler shift[6].

Quadrupole splitting

The quadrupole splitting data of Table 1 lie all in a very narrow range, and do not suggest the existence of two different structures. It can be seen that the only datum which is somewhat out of the line by a very small amount is the 2-CH_3, 3-Cl derivative.

Debye-Waller factors

In the present analysis we do not pretend to show exact figures for the recoilless fraction at different temperatures, but to show qualitatively its temperature dependence and the relation with different structures.

Several authors[14-18] have discussed the relations between areas of absorption peaks and recoilless fractions, and the importance of background corrections. The area A is proportional to the product of recoilless fractions f of course and absorber and to w the surface density of absorbing atoms and, if the absorber is not thin, to a saturation function.

If the solid is described by the Debye model the recoilless fraction f can easily be calculated in terms of the Debye temperature θ_D[19]. As an exact background correction cannot be performed but it is known that it is approximately constant, we have plotted in Fig. 4 $\ln(A/wf_s)$, using data for f_s, the recoilless fraction for the source, taken from ref. 19. As can be seen from the plot, all the data lie within the error which can be attributed to the measurement of the weight and area of the samples. This would suggest again that the structure remains constant, because otherwise we would expect, as described above, a change in the phonon distribution. From the slope of the high temperature part of the graph we obtain $\theta_D = 225° K$. This result should not

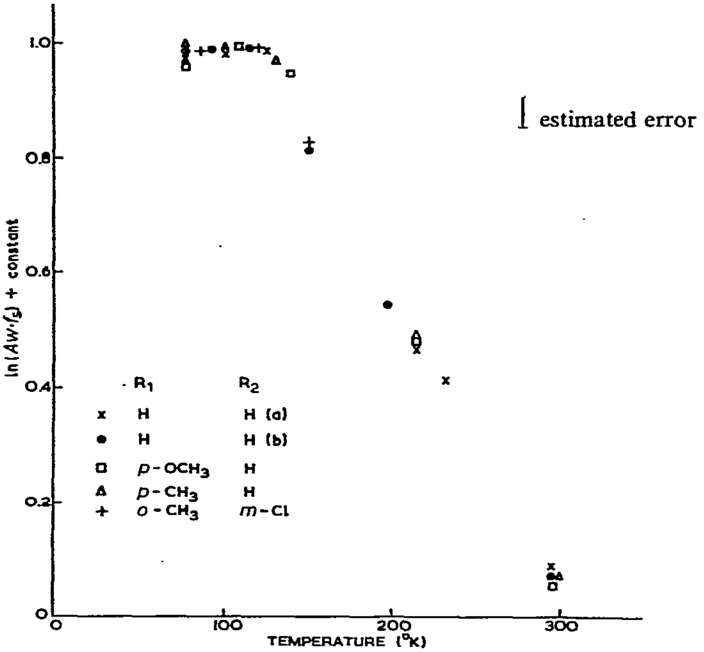

Fig. 4. Temperature dependence of $\ln(A/w \cdot f_s)$, for the different compounds (for the meaning of the abbreviations see text).

be taken too seriously, due to the limitations of Debye's theory in the description of a molecular solid.

CONCLUSIONS

We have tried to show in a qualitative way by means of the Mössbauer effect that the substituted iron nitrosocarbonyls all have the same structure regardless of the substituents attached to the phenyl group.

The problem which has been studied shows the advantages and limitations of Mössbauer spectroscopy as an independent structural tool. While X-ray diffraction studies have been made only on one derivative, due to the difficulty of growing large enough crystals, and have provided the complete structure on this sample, Mössbauer studies, which require less stringent limitations on the form of the samples, only establish the identity of the structures of the different derivatives but do not give information about the exact configurations.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. O. S. Mills, of the Department of Chemistry, Manchester University, for useful discussions and for showing us the results of his X-ray work prior to publication, and Dr. E. Koerner von Gustorf who generously provided the samples.

REFERENCES

1 E. Koerner von Gustorf, M. C. Henry, R. E. Sacher and C. Di Pietro, *Z. Naturforsch. B.*, 21 (1966) 1152.
2 E. O. Fischer, V. Kiener, D. St. P. Bunbury, E. Frank, P. F. Lindley and O. S. Mills, *Chem. Commun.*, (1968) 1378.
3 P. F. Lindley and O. S. Mills, *J. Chem. Soc. A*, (1969) 1279.
4 E. Frank and D. St. P. Bunbury, *J. Chem. Soc.*, to be published.
5 M. J. Barrow and O. S. Mills, *Angew. Chem. (Intern. Ed.)*, 8 (1969) 879.
6 V. I. Gol'danskii and R. H. Herber, *Chemical Applications of Mössbauer Spectroscopy*, Acad. Press, New York (1968).
7 N. N. Greenwood, *Chem. Brit.*, 3 (1967) 56.
8 H. Sano, M. Aratani and H. A. Stöckler, *Phys. Lett. A*, 26 (1968) 559.
9 A. Yu. Aleksandrov, O. Yu. Okhlobystin, L. S. Polak and V. S. Shpinel, *Dokl. Akad. Nauk. SSSR*, 157 (1964) 934.
10 G. K. Wertheim and R. H. Herber, *J. Amer. Chem. Soc.*, 84 (1962) 2274.
11 E. Frank, D. St. P. Bunbury, F. Mabbs and G. W. A. Newton, unpublished results.
12 T. Yoshioka, Y. Gohshi and H. Kohno, *Anal. Chem.*, 40 (1968) 603.
13 A. H. Muir, K. J. Ando and H. M. Coogan, *Mössbauer Effect Data Index 1958–1965*, Interscience, New York (1966).
14 S. Margulies and J. Ehrman, *Nucl. Instrum. Methods*, 12 (1961) 131.
15 R. S. Preston, S. S. Hanna and J. Herberle, *Phys. Rev.*, 128 (1962) 2207.
16 C. Lang, *Nucl. Instrum. Methods*, 24 (1965) 425.
17 R. M. Housley, N. E. Erickson and G. J. Dash, *Nucl. Instrum. Methods*, 27 (1964) 25.
18 R. M. Housley, *Nucl. Instrum. Methods*, 35 (1965) 77.
19 W. A. Steyert and R. D. Taylor, *Phys. Rev.*, 134A (1964) 716.