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Electron spin resonance spectroscopy of $Mn(CO)_5\cdot$ radicals generated in the gas phase thermolysis of $Mn_2(CO)_{10}$

Karel Mach, Jana Nováková

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 18223 Prague 8 (Czechoslovakia)

and J. Barrie Raynor

Department of Chemistry, University of Leicester, Leicester LE1 7RH (UK)

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Abstract

The $Mn(CO)_5\cdot$ radicals from the gas-phase thermolysis of $Mn_2(CO)_{10}$ were trapped in a co-condensed adamantane matrix at 77 K and shown to give an ESR spectrum not contaminated by signals from other paramagnetic species. The radicals were formed in a narrow range of temperatures, 342-388 K, with an optimum at 363 K. They were found to be thermally stable, and the strongly anisotropic ESR spectrum suggested that they were fixed without free rotational movement up to 213 K. The peroxo radical $Mn(CO)_5O_2\cdot$was trapped, either alone or together with $Mn(CO)_5\cdot$, in the presence of trace amounts of dioxygen.

Introduction

The $Mn(CO)_5\cdot$, radical has been suggested to play a substantial role in electrochemical and photochemical reactions of $Mn_2(CO)_{10}$ [1-5]. In none of the experiments was the $Mn(CO)_5\cdot$ radical observed by ESR spectroscopy, although clear evidence has been obtained for stable radical derivatives of $Mn(CO)_5\cdot$ produced by spin trapping techniques [6]. The alleged observation of $Mn(CO)_5\cdot$ radicals in the photolysis of $Mn_2(CO)_{10}$ in tetrahydrofuran (THF) [7,8] was later shown to refer to Mn^{II} species [9,10]. Furthermore, a Mn-containing radical found in the sublimate of $Mn_2(CO)_{10}$ [11] was later proved to be a peroxo radical $Mn(CO)_5O_2\cdot$ [12]. However, the $Mn(CO)_5\cdot$ radical has been prepared, and

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Correspondence to: Dr. K. Mach or Dr. J.B. Raynor stabilised in inert gas matrices; *e.g.* by the reaction of $Mn(CO)_5Br$ with sodium or silver atoms in argon in a rotating cryostat [13], by the co-condensation of Mn, CO and Ar on a cold finger [14], and by the photolysis of $Mn(CO)_5H$ in an argon matrix [15].

In this paper, we report the ESR spectrum of pure $Mn(CO)_5\cdot$ generated by the gas-phase thermolysis of $Mn_2(CO)_{10}$ and co-condensed with adamantane at 77 K.

Experimental

Commercial $Mn_2(CO)_{10}$ (Fluka) was sublimed *in vacuo* at 313 K to give a yellow crystalline product; both the crude and sublimed material were used for thermolytic experiments and yielded the same results. Adamantane (Fluka) was repeatedly sublimed *in vacuo* and degassed. A simple thermolytic glass and quartz all-sealed apparatus [16] was equipped with metal valves and Pirani and Penning ionisation gauges. The quartz tube pyrolyser (i.d. 0.5 cm, length 5 cm) was heated from the outside with resistance wire and its temperature in the middle part was measured by use of a Pt/PtRh (13%) thermocouple with accuracy of 0.01 mV (*ca.* 2 K). The apparatus was evacuated overnight to 1×10^{-4} Pa and the pyrolyser was preheated to the approximate temperature used for thermolysis. The thermolyses were performed at a constant vapour pressure of $Mn_2(CO)_{10}$ (0.15 Pa) and adamantane (9 Pa), with both storage vessels at room temperature, 295 K.

The admittance of vapours resulted in an increase in the pyrolyser temperature, while addition of liquid nitrogen into the Dewar vessel with trapping finger led to its decrease. The temperature was then only recorded, not corrected. Except for the first 10 min of the thermolysis when the temperature fell by *ca.* 10 K, it was constant to within 2 K. The duration of thermolysis was usually 60 min. The feeding valves were then closed, the heater was switched off, and the apparatus was left attached to the vacuum pump for 15 min. The Dewar vessel was sealed off and placed in the cavity of an ESR spectrometer (ERS-220, Centre for Scientific Instruments, German Academy of Sciences, Berlin). The g-values were determined relative to the signal of a Mn^{2+} ($M_I = -1/2$ line) standard at 1.9860 using a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). Spin Hamiltonian parameters were derived by spectrum simulation. Controlled warming of the sample was carried out by blowing cooled nitrogen into the finger of the Dewar vessel from a variable temperature unit (STT-3).

Evolution of CO at various temperatures of thermolysis was detected by mass spectrometry. For this purpose the pyrolytic apparatus was evacuated through a Finigan 400 quadrupole mass spectrometer and the thermolysis of $Mn_2(CO)_{10}$ was carried out in the absence of adamantane with the finger cooled by liquid oxygen.

Results and discussion

Thermolysis of vapours of $Mn_2(CO)_{10}$ yielded the trapped $Mn(CO)_5\cdot$ radical only in the narrow temperature range 342–388 K, with an optimum at 363 K. At lower and higher temperatures, no ESR spectrum was observed although the matrix was always yellow-coloured due to $Mn_2(CO)_{10}$. The ESR spectrum of the radical trapped in the adamantane matrix at 77 K (Fig. 1(A)) did not contain signals attributable to any other paramagnetic species, and so its parameters were

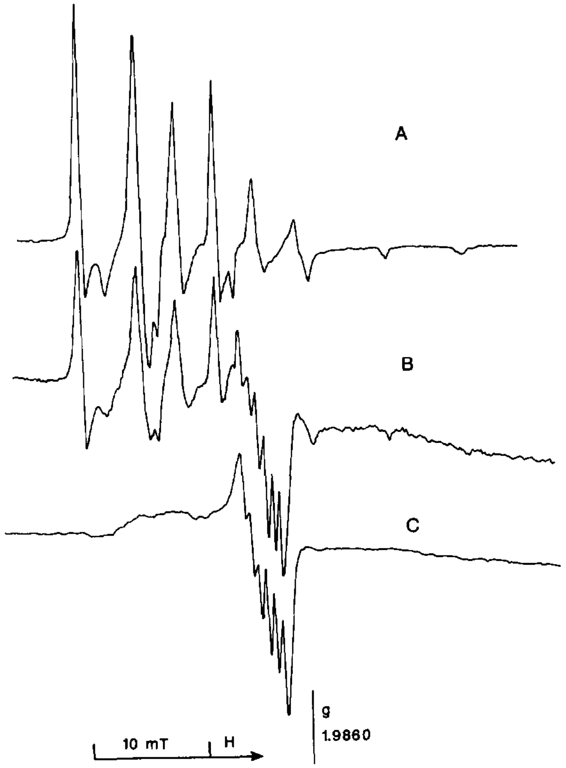

Fig. 1. ESR spectra of products from the gas-phase thermolysis at 363 K of $Mn_2(CO)_{10}$ (co-condensed adamantane matrix at 77 K, modulation amplitude 3G, microwave power 2mW). (A) $Mn(CO)_5\cdot$ (in absence of oxygen). (B) mixture of $Mn(CO)_5\cdot$ and $Mn(CO)_5O_2\cdot$ (in the presence of a trace of oxygen). (C) $Mn(CO)_5O_2\cdot$ (in the presence of 4×10^{-2} Pa oxygen).

determined with higher accuracy than previously [13,15] (see Table 1). As for the sign of the hyperfine coupling constants, we concur with previous assignments [13,15], *i.e.* $A_\parallel > 0$ and $A_\perp < 0$. It follows that A_{iso} would be 0 ± 1.5 G.

Table 1

ESR data for manganese(I) carbonyl radicals

	$g_\parallel$	$g_\perp$	$A_\parallel$/G	$A_\perp$/G	Ref.
$Mn(CO)_5\cdot$	-	-	±65.8	±32.8	14
	2.000±0.003	2.038±0.003	66.±3	−30. ±3	13
	2.004±0.010	2.043±0.010	65.±4	−33.5±2	15
	2.0011	2.0375	64.5	32.5	This work [a]
$Mn(CO)_5O_2\cdot$	-	-	22.5	6.75	11
	2.007	2.003	8.5	6.3	12
	2.061	2.0087	8.3 [b]	6.4	This work [a]

[a] *g* values and splitting constants are determined from spectra by simulation and include higher order effects. [b] estimated from linewidth *via* simulation.

Spectrum simulation correctly reproduces the anomalously intense lines $M_I = 5/2$ (parallel) and $M_I = 3/2$ (perpendicular) that had been noted by Symons and Sweaney [15] and arise from turning points in the angular variation of the powder spectra at angles other than 0 or 90 degrees to the principal axes.

The $Mn(CO)_5\cdot$ radical trapped in adamantane matrix was suprisingly stable: controlled warming of the sample in a thermal cycle from 77 to 213 K and back again resulted in only *ca.* 40% loss of the radical. Further warming to 233 K, however, led to rapid decay. During warming to 213 K, the ESR spectrum remained anisotropic although the lines were slightly broadened. This shows that a radical of this size cannot freely rotate in this very soft matrix, in contrast to smaller radicals [16–18].

The yield of $Mn(CO)_5\cdot$ radical was difficult to estimate because of the large width of the spectrum and high amplification of the signal, but it is low compared with yields of organic radicals we have previously obtained by the same method. This, as well as the relatively sharp maximum of the formation of $Mn(CO)_5\cdot$ at 363 K, may be due to a competitive mode of decomposition of $Mn_2(CO)_{10}$ with evolution of CO. The mass spectra of non-condensing thermolytic products at 77 K revealed that while no CO was evolved at 333 K, its maximum was already reached at 403 K. About 60% evolution of CO was observed at 363 K, the optimum temperature for the formation of $Mn(CO)_5\cdot$. This competition of two decomposition pathways yielding a) $Mn(CO)_5\cdot$ and products of its interaction with various substrates, and b) $Mn_2(CO)_9$ with a preserved Mn–Mn bond, is well known from the photochemistry of $Mn_2(CO)_{10}$ [1–5].

The presence of a deliberate very small leak of air into the thermolytic apparatus brought about the formation of a mixture of $Mn(CO)_5\cdot$ and $Mn(CO)_5O_2\cdot$ radicals (Fig. 1(B)). At a partial pressure of O_2 comparable to the pressure of $Mn_2(CO)_{10}$ (*ca.* 0.15 Pa), no radical was observed, probably due to further oxidation of the $Mn(CO)_5O_2\cdot$. The ESR hyperfine parameters for $Mn(CO)_5O_2\cdot$, which show a 6.4 G hyperfine coupling to Mn, agree with other results but the $g_\parallel$ feature is at variance with them. The large coupling $A_\parallel = 22.5$ [11] was probably due to the presence of traces of $Mn(CO)_5\cdot$. Values of $g_\parallel$ and $A_\parallel$ differing only slightly from the perpendicular values [12] do not account for the unresolved broad feature at lower magnetic field (Fig. 1(C)). This feature, although low in intensity, is readily seen when the radical $Mn(CO)_5$ is suppressed (Fig. 1). We believe this broad feature represents unresolved hyperfine structure of about 8.3 G on the $g_\parallel$ feature that is centred at about $g = 2.061$.

Closer inspection of the well resolved perpendicular lines shows they have the shape expected for typical perpendicular features rather than the almost isotropic lines expected if the parallel and perpendicular values of g and A were almost coincidental as others suggest [12]. This is supported by computer simulation. It would be surprising if $g_\parallel$ and $g_\perp$ were very close since in related radicals the difference is quite large, *viz.* O_2^-: $g_\parallel = 2.175$, $g_\perp = 2.00$ [19]; $HOO\cdot$: $g_\parallel = 2.035$, $g_x = 2.008$, $g_y = 2.004$ [20]; and typical $CoOO\cdot$: $g_\parallel = 2.07$, $g_\perp = 2.00$ [21].

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References

1 D.J. Stufkens, Coord. Rev., 104 (1990) 39.
2 K. Yasufuku, N. Hiraga, K. Ichimura and T. Kobayashi, Coord. Chem. Rev., 97 (1990) 167.
3 P.H. Rieger, NATO ASI Ser., Ser. C, 257 (1989) 375.
4 T.J. Meyer and J.V. Caspar, Chem.-Rev., 85 (1985) 187.
5 A.E. Stiegman and D.R. Tyler, Coord. Chem. Rev., 63 (1985) 217.
6 A. Vleck, Jr., J. Organomet. Chem., 306 (1986) 63 and references therein.
7 S.A. Hallcock and A. Wojcicki, J. Organomet. Chem., 54 (1973) C27.
8 C.L. Kwan and J.K. Kochi, J. Organomet. Chem., 101 (1975) C9.
9 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Organomet. Chem., 92 (1975) C11.
10 A. Hudson, M.F. Lappert, J.J. MacQuitty, B.K. Nicholson, S.W. Bratt and M.C.R. Symons, J. Organomet. Chem., 110 (1976) C5.
11 E.O. Fischer, E. Offhaus, J. Muller and D. Nothe, Chem. Ber., 105 (1972) 3027.
12 S.A. Fieldhouse, B.W. Fullam, G.W. Neilson and M.C.R. Symons, J. Chem. Soc., Dalton Trans., (1974) 567.
13 J.A. Howard, J.R. Morton and K.F. Preston, Chem. Phys. Lett., 83 (1981) 226.
14 G.A. Ozin, personal communication quoted by A.S. Huffadine; B.M. Peake, B.M. Robinson, J. Simpson and P.A. Dawson, J. Organomet. Chem., 121 (1976) 391.
15 M.C.R. Symons and R.L. Sweany, Organometallics, 1 (1982) 834.
16 K. Mach, J. Nováková and Z. Dolejšek, Coll. Czech. Chem. Commun., 49 (1984) 1325.
17 K. Mach, J. Nováková, V. Hanuš and Z. Dolejšek, Coll. Czech. Chem. Commun., 51 (1986) 2675.
18 K. Mach, J. Nováková, V. Hanuš and J.B. Raynor, Tetrahedron., 45 (1989) 843.
19 J.E. Bennett, D.J.E. Ingram, M.C.R. Symons, P. George and J.S. Griffiths, Phil. Mag., 46 (1955) 443; W. Kanzig and M.H. Cohen, Phys. Rev. Letters, 3 (1959) 509.
20 R.C. Catton and M.C.R. Symons, J. Chem. Soc. (A), (1969) 1393.
21 J.B. Raynor, R.D. Gillard and J.D. Pedrosa de Jesus, J. Chem. Soc. Dalton Trans. (1982) 1165; J.B. Raynor, Inorg. Nucl. Chem. Lett., 10 (1974) 867 and references therein.