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## Preliminary Communication

### Photochemistry of methanesulphinatopentacarbonylmanganese, $\text{Mn}(\text{CO})_5(\text{SO}_2\text{CH}_3)$ , in frozen gas matrices at *ca.* 12 K

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#### Abstract

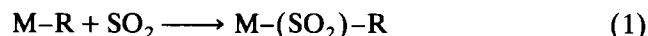
Infrared spectroscopic evidence is presented which shows that photolysis of the *S*-sulphinato complex,  $\text{Mn}(\text{CO})_5(\text{S}-\text{SO}_2\text{CH}_3)$ , in argon, methane, dinitrogen and carbon monoxide matrices at *ca.* 12 K produces first the *O*-sulphinato complex,  $\text{Mn}(\text{CO})_5(\text{O}-\text{SO}_2\text{CH}_3)$ , which on further photolysis is converted into the *O,O'*-sulphinato complex,  $\text{Mn}(\text{CO})_4(\text{O},\text{O}'-\text{SO}_2\text{CH}_3)$  with ejection of a CO ligand. Annealing the matrices to *ca.* 35 K results in reversal of the *O,O'*-sulphinato complex to the parent *S*-sulphinato complex.

One of the most important reactions of metal hydride and metal alkyl complexes is the so called "insertion reaction" in which a ligand, X, is "inserted" to give M–X–R complexes, where R is H or alkyl. Some examples of X are CO, olefins, acetylenes,  $\text{CO}_2$  and  $\text{SO}_2$  [1]. Some insertion reactions are reversible, *e.g.* carbonylation and decarbonylation for CO and insertion and  $\beta$ -elimination for olefins. In the case of the reactions involving CO the carbonylation and decarbonylation reactions appear to go through a common intermediate, *e.g.*  $\text{Mn}(\text{CO})_4(\text{COCH}_3)$  for  $\text{Mn}(\text{CO})_5(\text{CH}_3)$  and  $\text{Mn}(\text{CO})_5(\text{COCH}_3)$ , according to the principle of microscopic reversibility [2,3].

Matrix isolation studies have been very successful in characterisation of reactive organometallic species that have been proposed in reaction pathways [4]. For example, photolysis of  $\text{Mn}(\text{CO})_5(\text{COCH}_3)$  in frozen gas

matrices at *ca.* 12 K led to the trapping of  $\text{Mn}(\text{CO})_4(\text{COCH}_3)$  and its subsequent conversion to  $\text{Mn}(\text{CO})_5(\text{CH}_3)$  [2], while for  $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{C}_2\text{H}_5)$  complexes, where M is Mo or W,  $\beta$ -elimination was shown to be preceded by CO loss to give  $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_2\text{H}_5)$ , a 16-electron species with a vacant site available for the migration step to give  $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_2\text{H}_4)(\text{H})$  [5].

We describe here a study of  $\text{Mn}(\text{CO})_5(\text{S}-\text{SO}_2\text{CH}_3)$  by matrix isolation spectroscopy aimed at exploring the  $\text{SO}_2$  insertion pathways for M–R complexes (eq. (1)) [6,7], and the subsequent breakdown, if any, of the M– $\text{SO}_2$ R fragment. For example, in contrast to the ejection of CO from acyl complexes,  $\text{SO}_2$  ejection from sulphinato complexes seems to be a relatively minor pathway compared to loss of  $\text{R}^*$  [8–12]:



The IR spectra of  $\text{Mn}(\text{CO})_5(\text{S}-\text{SO}_2\text{CH}_3)^*$  [13] isolated at high dilution in argon, dinitrogen, methane and carbon monoxide matrices \*\* all showed similar band patterns. For example in  $\text{N}_2$  matrices there are five absorption bands in the terminal CO-stretching region at 2141 (A'), 2094 (A'), 2055 (A'), 2044 (A'), and *ca.* 2025 (A'; matrix splitting)  $\text{cm}^{-1}$  for a molecular symmetry reduced from  $C_{4v}$  local symmetry to one not higher than  $C_s$ , owing to the presence of the  $\text{RSO}_2$  moiety, a broad band at 1986  $\text{cm}^{-1}$  corresponding to the mono-enriched  $^{13}\text{CO}$  species present in natural abundance, and three bands at 1234, 1219, 1072  $\text{cm}^{-1}$ , due to the  $\text{SO}_2$  ligand with the *S*-sulphinato structure I [15] [Fig. 1(a) and Table 1].

On irradiation in  $\text{N}_2$  matrices with filtered UV-vis radiation ( $310 < \lambda < 390$  nm), corresponding to the low energy tail of the absorption band of the parent complex ( $\lambda_{\text{max}} = 288$  nm), seven new bands grew in at 2114, 2039, 2021, 1996, 1981, 1220 and 975  $\text{cm}^{-1}$  while the bands of the parent compound decreased in intensity [Figs. 1(b), (c) and Table 2]. On extended visible irradiation, corresponding to the tail of the new product band ( $\lambda_{\text{max}} = 395$  nm) there was no reversal of the

\* The sample, provided by Professor A. Wojcicki [13] gave a satisfactory parent ion by FAB mass spectroscopy prior to matrix isolation studies.

\*\* Details of the matrix isolation equipment at Southampton have been described elsewhere, as have the filters used for wavelength-selective photolysis [14].

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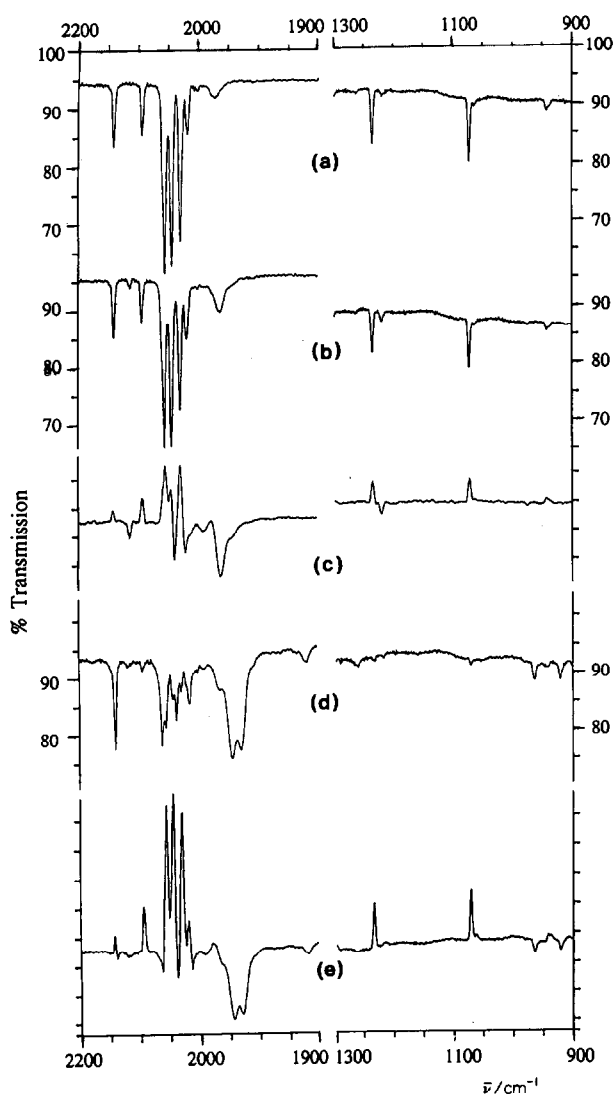


Fig. 1. Infrared spectra from an experiment with  $Mn(CO)_5(S-SO_2CH_3)$  isolated in a nitrogen matrix at ca. 12 K: (a) after deposition, (b) after 5 min irradiation ( $310 < \lambda < 390$  nm), (c) subtraction spectrum [(b)-(a)], (d) after 95 min irradiation ( $310 < \lambda < 390$  nm), (e) subtraction spectrum [(d)-(a)].

primary photoreaction, such as is commonly found for other metal carbonyl complexes which have ejected a CO ligand [4]. On the basis of several features, *e.g.* the similar results in Ar,  $N_2$ ,  $CH_4$  and CO matrices and observations that (i) no “free” CO was detected initially, (ii) no incorporation of  $N_2$  took place in  $N_2$  matrices, (iii) there was no suppression of the primary photoprocess in CO matrices, and (iv) the band pattern in the lower region changed from one due to structure I to one consistent with structure III [15], it can be concluded that the most probable structure for the new

TABLE 1. Infrared band positions ( $cm^{-1}$ ) for  $Mn(CO)_5(S-SO_2CH_3)$

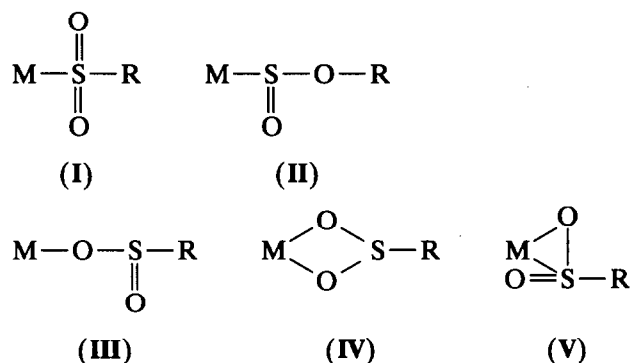
$CCl_4^a$	$N_2^b$	Ar <sup>b</sup>	CO <sup>b</sup>	$CH_4^b$
				2146w-sh
2139w-m	2141m	2139m	2141s	2139m
2090w	2094m	2092m	2092s	2093s
2059s	2055s	2054s		2057s
				2053s
2044s	2044s	2042s	2042s	2040s
2027m	2029s <sup>c</sup>	2027s <sup>c</sup>	2028s <sup>c</sup>	2023s <sup>c</sup>
	2018m	2018m	2016m	2016m
1201s	1234m	1245m	1222m	1232m
1182sh	1219w	1227w		1217vw
1053s	1072m	1078m	1062m	1070m
1044sh				1060vw

<sup>a</sup> Solution date from ref. 13.

<sup>b</sup> Band ( $cm^{-1}$ ) for  $Mn(^{12}CO)_4(^{13}CO)(S-SO_2CH_3)$  observed in natural abundance at 1986 ( $N_2$ ), 1986 (Ar), 1983 (CO), 1983 ( $CH_4$ ).

<sup>c</sup> Matrix split band.

species is methane-*O*-sulphinato-pentacarbonylmanganese,  $Mn(CO)_5(O'-SO_2CH_3)$ .



On further irradiation ( $310 < \lambda < 390$  nm) the above seven new bands were replaced by eight new bands at 2139 (“free CO”), 2062, 2037, 2013, 1972, 1964, 964 and  $921\text{ cm}^{-1}$  [Figs. 1(d), (e) and Table 3]. Although CO had been ejected, no photochemical reversal was observed. On the basis of analogous observations in the four matrices (Table 3), the detection of “free” CO, the shift of the carbonyl band pattern to significantly lower wavenumbers, and the correlation of the sulphi-

TABLE 2. Infrared band positions ( $cm^{-1}$ ) for  $Mn(CO)_5(O-SO_2CH_3)$

$N_2$	Ar	CO	$CH_4^a$
2114w	2111w	2113w	2111w
2039s	2037s	2038s	2038w
			2034w
2021s	2014s	2019s	2014s
1996w	1994w	1996w	1990w
1981s	1981s	1980s	1975s
1220w	1228w	1212w	1215w
975w	974w	973w	973w

<sup>a</sup> Additional very weak band at  $1964\text{ cm}^{-1}$  (see Table 3).

TABLE 3. Infrared band positions ( $cm^{-1}$ ) for  $Mn(CO)_4(O, O'-SO_2CH_3)$ 

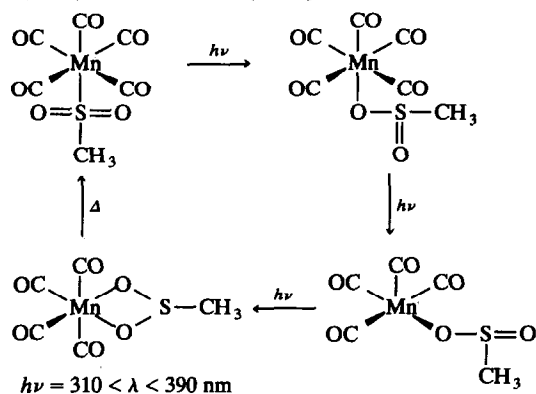
$N_2^a$	Ar <sup>a</sup>	CO <sup>a</sup>	$CH_4^a$
2062m	2072w	2063s	2062w
2037m	2035s	2037s	2034m
2013m	2013s	2013s	2011m
1972s	1969s	1969s	1974sh
1964s			1965s
964w	962w	962w	960w
921w	922w	920w	918w

<sup>a</sup> Additional very weak band ( $cm^{-1}$ ) at: 1996w, 1982w, 1909w ( $N_2$ ); 2113m, 1995w, 1981w, 1950, 1908w (Ar); 1994w, 1908w (CO); 2115w, 1989m, 1946m, 1906w ( $CH_4$ ).

nato band pattern with that for structure IV [15], the second product is judged to be methane- $O, O'$ -sulphinatotetracarbonylmanganese,  $Mn(CO)_4(O, O'-SO_2CH_3)$ .

It is of interest that on warming of the matrix to ca. 35 K the new bands due to the  $Mn(CO)_4(O, O'-SO_2CH_3)$  species and the "free" CO band decrease in intensity while the bands for  $Mn(CO)_5(S-SO_2CH_3)$  increase in intensity. This indicates that  $Mn(CO)_4(O, O'-SO_2CH_3)$  can react thermally with CO.

The series of reactions for  $Mn(CO)_5(S-SO_2CH_3)$  in low temperature media, shown in Scheme 1, indicate that the methanesulphinato group is retained in contrast to the loss of  $CH_3^{\ominus}$  in solution [13] and the loss of  $CH_3^{\ominus}$  to yield  $Mn(CO)_5(SO_2)^+$  as the primary fragmentation ion in the mass spectra. The retention of the sulphinato group is also in contrast to the ejection of CO from an acetyl group [2]. The absence of evidence for  $CH_3^{\ominus}$  loss is perhaps not surprising given the close proximity of the ejected  $CH_3^{\ominus}$  and  $Mn(CO)_5(SO_2)^{\bullet}$  radicals in a tight matrix cage; cf. the failure to detect radicals in the case of various M-M bonded dimers in



Scheme 1.

low temperature matrices [16]. The observation of rearrangements, however, begins to give some insights into the insertion reaction. The  $O'$  to  $O', O'$  rearrangement is particularly interesting, and raises the question of why the 16 electron species,  $Mn(CO)_4(O'-SO_2CH_3)$  was not detected. On the basis of the photochemistry of  $M(CO)_5(\eta^1-C_7H_7)$  ( $M = Mn, Re$ ), where vacant sites were "captured" by "spare" olefinic ligands within the complex [17], the answer would appear to be that the available O donor of the sulphinato ligand captured the vacant site in the 16-electron complex.

Further work with other sulphinato metal complexes will be carried out to see whether the retention of the methanesulphinato ligand observed above is a general process.

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