Intermediacy of *O*-Sulphinates in the Reaction of Transition-Metal Carbonyl Alkyls and Aryls with Sulphur Dioxide

By S. E. JACOBSON, P. REICH-ROHRWIG, and A. WOJCICKI*
(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

Summary Spectroscopic (^{1}H n.m.r. and i.r.), electrical conductivity, and chemical evidence indicates that reactions of π-$C_5H_5Fe(CO)_2R$, π-$C_5H_5Mo(CO)_3R$, and $Mn(CO)_5R$ (R = alkyl or aryl) with SO_2 proceed *via* the intermediacy of the oxygen-bonded sulphinates, which subsequently rearrange to the thermodynamically stable and isolable sulphur-bonded sulphinates.

THE reaction of sulphur dioxide with a variety of transition-metal alkyls and aryls serves as a convenient route to the corresponding *S*-sulphinates.[1-3] It has been assumed—in some cases implicitly—that the *S*-bonded sulphinates are formed directly *via* a one-step concerted mechanism.[1,3] We now present results which show that, contrary to the earlier suppositions, oxygen-bonded sulphinates are the initial products in some, if not all, reactions of SO_2 with transition-metal alkyls and aryls.

Changes in constitution of a solution of π-$C_5H_5Fe(CO)_2CH_2Ph$ in liquid SO_2 were followed by n.m.r. spectroscopy at $-18°$. In the methylene proton region, the CH_2 signal of π-$C_5H_5Fe(CO)_2CH_2Ph$ at τ 7·31 diminishes in intensity and a quartet and a singlet appear and grow at τ 6·49 (centre) and 5·79. The latter is due to the CH_2 protons of π-$C_5H_5Fe(CO)_2S(O)_2CH_2Ph$.[4] After *ca.* 1 h the spectrum is that shown in the Figure. Longer reaction times (*ca.* 1 day at $-25°$) cause diminution in intensity of the signal at τ 6·49 and disappearance of the signal at τ 7·31. Removal of the solvent at approximately this stage of the reaction leads to isolation of the *S*-bonded π-$C_5H_5Fe(CO)_2S(O)_2CH_2Ph$.

A qualitatively similar behaviour is noted for a solution of $Mn(CO)_5CH_2Ph$ in SO_2 at $-37°$. However, in the n.m.r. spectrum of π-$C_5H_5Mo(CO)_3CH_2Ph$, recorded in SO_2 at $-37°$, a very low intensity quartet centred at τ 6·40 appears at the outset, remains barely discernible throughout the reaction, and eventually vanishes. For all three benzyl complexes the observed behaviour is consistent with a two step reaction:

$$[M]\text{-}CH_2Ph + SO_2 \xrightarrow{k_1} \text{Intermediate} \xrightarrow{k_2} [M]\text{-}SO_2{\cdot}CH_2Ph$$

with k_2/k_1 decreasing in the order $[M] = \pi$-$C_5H_5Mo(CO)_3 > Mn(CO)_5 > \pi$-$C_5H_5Fe(CO)_2$. The spectra are presented in the Table.

TABLE

N.m.r. data (τ) for CH_2 *protons of* [M]–CH_2Ph *and the corresponding* O- *and* S-*sulphinates in* SO_2[a]

[M]	Temp.	CH_2Ph	$OS(O)CH_2Ph$	$S(O)_2CH_2Ph$
π-$C_5H_5Fe(CO)_2$	−18°	7·31	6·57, 6·41(*J* 12·6 Hz)	5·79
π-$C_5H_5Mo(CO)_3$	−37°[b]	7·12	6·49, 6·31(*J* 12·5 Hz)	5·78
$Mn(CO)_5$	−37°[b]	7·64	6·41, 6·27(*J* 12·5 Hz)	5·70

[a] Me_4Si internal reference. Accuracy *ca.* 0·03 p.p.m. [b] ±7°.

The i.r. spectrum in the ν(CO) region of a solution of π-$C_5H_5Fe(CO)_2CH_2Ph$ in SO_2, recorded 4 h after its preparation at −30°, shows, in addition to the weaker bands of the unchanged alkyl, two intense absorptions at 2062 and 2012 cm^{-1}. These frequencies are very close to, but not identical with, those (2064 and 2018 cm^{-1}) obtained for a solution of the authentic *S*-bonded π-$C_5H_5Fe(CO)_2S(O)_2CH_2Ph$ at the same temperature. They have been assigned to the reaction intermediate. SO_2 solutions of π-$C_5H_5Fe(CO)_2R$ (R = Me, *p*-Tol) manifest a similar behaviour, indicating that this phenomenon is general and extends also to the aryl complexes. A close similarity in ν(CO) between the intermediates and the corresponding *S*-sulphinates and/or small concentrations of the former in solution helped preclude earlier detection of this behaviour.

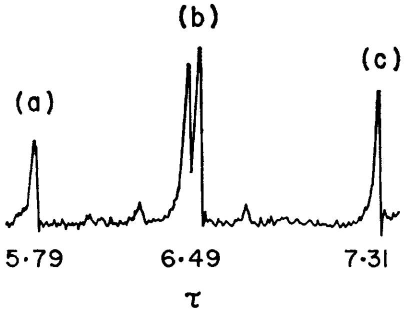
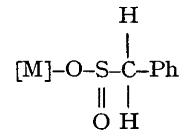


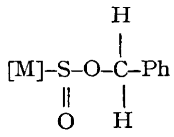
FIGURE. *The* CH_2 *resonances of the* ^1H *n.m.r. spectrum of* ca. 1 *h old solution of* π-$C_5H_5Fe(CO)_2CH_2Ph$ *in* SO_2 *at* −18°: S- *sulphinate,* $S(O)_2CH_2$, (b) O-*sulphinate,* $OS(O)CH_2$, *and* (c) *unchanged alkyl,* $FeCH_2$.

The appearance of the CH_2 signals as AB quartets in the n.m.r. spectra of the benzyl intermediates points to a chiral sulphur therein.[5] Two structures (I and II) satisfy this requirement. Ionic formulations may be ignored, since solutions (*ca.* 10^{-2}M) of π-$C_5H_5Fe(CO)_2R$ (R = Me, CH_2Ph) in SO_2 at −32° exhibit molar conductivities of 0·24—0·11 ohm^{-1} cm^2, compared with 84 ohm^{-1} cm^2 for $[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]^+PF_6^-$.[6] Although the i.r. data do not permit differentiation between structures (I) and (II),[7] the former receives support from the following combined evidence. (i) A solution of π-$C_5H_5Fe(CO)_2R$ (R = Me, CH_2Ph, *p*-Tol; 1 part) in SO_2 was allowed to reflux for 2—4 h and then treated with KI (1—100 parts). After the resulting mixture was stored for *ca.* 2 h at −10°, removal of the solvent and work-up invariably led to isolation of π-$C_5H_5Fe(CO)_2I$ (up to 75%) in addition to the *S*-sulphinate. Since the *S*-sulphinates do not react with KI under these conditions, it is improbable that the *S*-bonded compounds of structure (II) would exhibit such a marked reactivity toward iodide. (ii) The direction of polarization of the M–R and S–O bonds renders the 1,2-addition to give MS(O)OR very unlikely. By contrast, the other mode of 1,2-addition to afford MOS(O)R is very plausible and occurs with a wide variety of main-group alkyls and aryls.[1]

Work in progress is concerned with isolation of *O*-sulfinato-intermediates.


$$[\mathrm{M}]\!-\!\mathrm{O}\!-\!\underset{\displaystyle\mathrm{O}}{\underset{\|}{\mathrm{S}}}\!-\!\overset{\displaystyle\mathrm{H}}{\overset{|}{\underset{\displaystyle\mathrm{H}}{\underset{|}{\mathrm{C}}}}}\!-\!\mathrm{Ph}$$

(I)


$$[\mathrm{M}]\!-\!\underset{\displaystyle\mathrm{O}}{\underset{\|}{\mathrm{S}}}\!-\!\mathrm{O}\!-\!\overset{\displaystyle\mathrm{H}}{\overset{|}{\underset{\displaystyle\mathrm{H}}{\underset{|}{\mathrm{C}}}}}\!-\!\mathrm{Ph}$$

(II)

[M] = π-$C_5H_5Fe(CO)_2$, π-$C_5H_5Mo(CO)_3$, $Mn(CO)_5$

We thank the National Science Foundation for support, The Ohio State University Graduate School for a Postdoctoral Fellowship (to P.R.-R.), and Mr. D. L. Denton for experimental assistance.

(*Received, September* 13*th*, 1971; *Com.* 1599.)

[1] W. Kitching and C. W. Fong, *Organometallic Chem. Rev.* (*A*), 1970, **5**, 281.
[2] M. D. Johnson and G. J. Lewis, *J. Chem. Soc.* (*A*), 1970, 2153.
[3] M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, 1970, **4**, 347.
[4] J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 1966, **88**, 4862.
[5] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Macmillan, New York, 1959, pp. 99–103.
[6] For other examples see P. J. Elving and J. M. Markowitz, *J. Chem. Educ.*, 1960, **37**, 75.
[7] E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, 1971, **10**, 1673.