

Photo-induced tautomerisation of methyltrioxorhenium(VII): the intermediate in olefin metathesis?

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Matrix-isolated $[\text{CH}_3\text{ReO}_3]$ tautomerises to $[\text{H}_2\text{C}=\text{Re}(\text{O})_2\text{OH}]$ under the influence of UV light; the carbene has been characterised in its normal and ^2H - and ^{13}C -enriched isotopic forms by its IR spectrum with results well replicated by quantum chemical calculations.

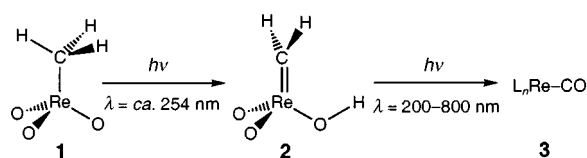
Since methyltrioxorhenium(VII), $[\text{CH}_3\text{ReO}_3]$ **1**, was first described, its rôle in promoting and catalysing numerous organic reactions has been explored in detail.^{1,2} In fact, **1** is probably the most widely active organometallic catalyst reported to date. This activity encompasses two general areas: (i) oxidation reactions (including olefin epoxidation, Baeyer–Villiger and aromatic oxidation);^{2–5} and (ii) olefin isomerisation and metathesis.⁶ The peroxo derivatives of **1** active in many reactions of type (i) have been isolated and characterised both structurally and spectroscopically.⁷ By contrast, the species responsible for catalytic activity of type (ii) have eluded direct detection, although a tautomer of the form $[\text{H}_2\text{C}=\text{Re}(\text{O})_2\text{OH}]$ **2**, has long been presumed to be the active form of **1**.^{2,8} There are numerous reports of rhenium–carbon multiple bonds in the literature generally, but not exclusively, involving rhenium in formal oxidation states $< +7$.^{8,9}

Photolysis of **1** in solution appears to result in homolysis of the Re–C bond.¹⁰ Our studies reveal, however, that the matrix-isolated molecule exhibits altogether different behaviour, initially tautomerising to the previously unknown carbene derivative **2** under the influence of UV light at wavelengths near 254 nm (Scheme 1). Tautomer **2** is also photolabile, broad-band UV–VIS irradiation ($\lambda = 200\text{--}800$ nm) causing it to decay to a product containing an Re–CO fragment, **3**, possibly $[\text{H}_2\text{Re}(\text{O})(\text{OH})\text{CO}]$.

Exposure of **1** isolated in an Ar matrix at 14 K to UV radiation with $\lambda = ca.$ 254 nm for several minutes results in the decay of the IR absorptions due to **1** and the simultaneous appearance and growth of new absorptions apparently due to a single product **2** (Fig. 1). Irradiation of the matrix with broad-band UV–VIS light ($\lambda = 200\text{--}800$ nm) was observed to cause the evolution from **2** of at least one further product **3** which could not be conclusively identified by its IR spectrum. The IR bands identified on the evidence of their growth-decay patterns enable **2** to be characterised as $[\text{H}_2\text{C}=\text{Re}(\text{O})_2\text{OH}]$, the conclusions being underpinned (i) by the observed effects of ^2H - and ^{13}C -

enrichment of the products derived from the species $[\text{CD}_3\text{ReO}_3]$ **1**- d_3 , and $[\text{C}^{13}\text{CH}_3\text{ReO}_3]$ **1**- ^{13}C , (ii) by parallels with the spectra of related carbene and Re=O derivatives, *e.g.* CoCH_2 ¹¹ and ReO_2F_3 ,¹² and (iii) by comparisons with the results of Density Functional Theory (DFT) calculations. (Calculations were carried out in Gaussian 98¹³ with geometries optimised at the BPW91/LANL2DZ level of theory; standard 6-31G(d,p) basis sets were used for C, O and H, whilst the Re basis set was augmented with an additional f-type polarisation function.) Prominent among its IR absorptions were those at 3650.0, 992.2, 963.3 and 668.4 cm^{-1} which are identifiable by their frequencies, intensities and responses to ^2H - and ^{13}C -enrichment with the modes $\nu(\text{O-H})$, $\nu_s(\text{Re=O})$, $\nu_{as}(\text{Re=O})$ and $\nu(\text{Re-OH})$, respectively. The presence of the Re=CH₂ unit is signalled by bands at 3079.6, 2985.8, 1320.9, 778.8, 756.4 and 627.9 cm^{-1} which we associate with the modes detailed in Table 1; each assignment is attested by analogy with the corresponding mode of CoCH_2 ¹¹ and by the ^2H and ^{13}C isotopic shifts, although the description of the motion is sometimes less than exact. The spectrum is well simulated by a scaled force field computed for **2** on the basis of DFT calculations (Table 1), the 36 frequencies measured for **2**, **2**- d_3 and **2**- ^{13}C being matched with an r.m.s. deviation of only 1.66%. It is also evident that mixing of the $\nu(\text{Re=C})$, $\rho(\text{CH}_2)$ and $\delta(\text{OH})$ motions complicates the interpretation of the spectrum in the region 600–800 cm^{-1} , preventing the identification of any one feature with the $\nu(\text{Re=C})$ mode. The relative intensities of the bands due to the well defined modes $\nu_{as}(\text{Re=O})$ and $\nu_s(\text{Re=O})$ imply an O=Re=O angle in the order of 116°, in good agreement with the optimum geometry computed for **2**.

Similar experiments with $[\text{CH}_2\text{DReO}_3]$ **1**- d_1 give rise not only to $[\text{H}_2\text{C}=\text{Re}(\text{O})_2\text{OD}]$, but also to the isotopomer



Scheme 1

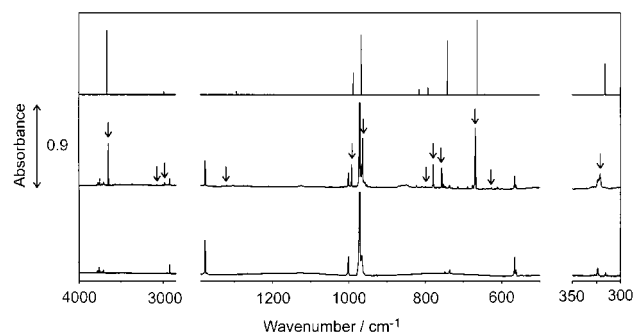


Fig. 1 (a) IR spectrum of $[\text{CH}_3\text{ReO}_3]$ **1** isolated in an argon matrix at 14 K; (b) IR spectrum showing the effect of irradiation at $\lambda = 254$ nm for 15 min (\downarrow indicates a feature associated with $[\text{H}_2\text{C}=\text{Re}(\text{O})_2\text{OH}]$ **2**); and (c) the spectrum of **2** based on the results of DFT calculations.

Table 1 Observed and calculated fundamental vibrational frequencies for **2**, **2**-¹³C, and **2**-*d*₃ under C_s symmetry. Observed and calculated intensities are in parentheses^a

H ₂ ¹² CrReO ₂ (OH)		H ₂ ¹³ CrReO ₂ (OH)		D ₂ ¹² CrReO ₂ (OD)		Description of mode
Obs.	Calc. ^b	Obs.	Calc. ^b	Obs.	Calc. ^b	
3650.0 (100)	3669.6 (87)	3650.4 (100)	3669.6 (87)	2694.2 (73)	2672.3 (63)	ν(O–H)
2985.8 (3)	2994.4 (5)	2980.2 (4)	2989.0 (5)	2195.1 (5)	2171.4 (6)	ν _s (CH ₂)
1320.9 (2)	1295.0 (5)	1311.8 (2)	1286.7 (5)	1009.9 (2)	1018.8 (6)	δ̇(CH ₂)
992.2 (25)	988.4 (30)	991.9 (26)	988.3 (30)	992.2 (31)	987.1 (42)	ν _s (ReO ₂)
799.2 (2)	815.4 (8)	798.7 (3)	812.4 (9)	622.6 (3)	631.0 (3)	δ̇(O–H) + ρ(CH ₂) + ν(Re=C) + ν(Re–OH)
778.8 (34)	792.0 (10)	768.3 (53)	770.4 (14)	578.9 (43)	556.8 (81)	
756.4 (30)	741.9 (73)	739.6 (19)	736.5 (67)	685.9 (10)	698.2 (6)	
668.4 (83)	664.2 (100)	668.8 (87)	664.2 (100)	660.0 (69)	664.7 (75)	
^c	286.4 (2)	^c	286.4 (2)	^c	286.0 (2)	
^c	255.6 (1)	^c	255.6 (1)	^c	252.7 (2)	ReO ₂ scissor
^c	239.8 (3)	^c	239.8 (3)	^c	217.6 (3)	δ̇(CReOH)
3079.6 (3)	3091.9 (0.6)	3068.4 (1)	3079.5 (0.6)	2315.2 (1)	2299.0 (0.3)	ν _{as} (CH ₂)
963.3 (64)	967.2 (81)	963.4 (80)	967.1 (81)	961.8 (100)	965.0 (100)	ν _{as} (ReO ₂)
627.9 (3)	644.2 (1)	625.7 (5)	639.3 (2)	500.2 (2)	504.1 (0.3)	CH ₂ scissor
^c	526.4 (0.2)	^c	525.8 (0.2)	^c	386.1 (0.01)	CH ₂ wag
321.2 (33)	315.9 (42)	320.7 (38)	315.2 (43)	239.3 (19)	253.4 (6)	δ̇(O–H)
^c	266.8 (15)	^c	266.8 (15)	^c	237.3 (15)	δ̇(CReO ₂)
^c	233.2 (0.03)	^c	233.2 (0.03)	^c	208.5 (16)	d(CReO ₂)

^a Frequencies in cm⁻¹; all intensities normalised to that of the most intense band set equal to 100 (in parentheses). ^b Calculated frequency scaled by a factor of 0.9740. The r.m.s. deviation between observed and scaled calculated frequencies is 1.66%. ^c Indicates a feature too weak to be observed.

[H(D)C=Re(O)₂OH] **2**-*d*₁. Here the ν(C–H) fundamental is isolated from all other modes in the molecule and so gives access, in principle, to relatively precise estimates of the dimensions of the CH₂ unit.¹⁴ The measured value of ν^{as}(C–H) (3035.4 cm⁻¹), taken together with ν(¹²C–H), ν(¹³C–H) and ν(¹²C–D) data for the other isotopomers, affords values that tally with the results of the DFT optimisations given in parentheses: *r*₀ = 1.088 Å (*r*_e = 1.099 Å), ∠HCH = 119 ± 4° (∠_eHCH = 115.8°).

Although **2** was formed almost exclusively when matrix-isolated **1** was photolysed at wavelengths near 254 nm, exposure to broad-band UV–VIS light gave rise to a secondary change. The sole detectable product **3** formed from **2** under these conditions, but always in the presence of an abundance of **1** and **2**, could be identified by a single IR band at 2051.4 cm⁻¹. Assignment to the ν(C–O) mode of an Re–CO moiety is strongly urged by a minimal change of frequency when **3** is formed from **1**-*d*₃ or **1**-*d*₁ but by a shift to 2003.8 cm⁻¹ when it is formed from **1**-¹³C. The circumstances preclude positive identification, but a possible candidate for **3** is the novel rhenium(v) compound [H₂Re(CO)(O)OH] formed by photoisomerisation of [H₂C=Re(O)₂OH] in a change that would parallel the conversion of [H₂COSi] to [H₂Si:CO].¹⁵ DFT calculations provide some support for [H₂Re(CO)(O)OH], finding a potential energy minimum 126 kJ mol⁻¹ above that of [H₂C=Re(O)₂OH] with a structure approximating to a square-based pyramid having the unique oxide ligand at the apex, and a calculated ν(C–O) frequency of 2040 cm⁻¹ (¹²C/¹³C shift = 44.5 cm⁻¹).

[CH₃ReO₃] is active in olefin metathesis only when activated by a co-catalyst (S₄N₄/AlCl₃), or when supported on silica or alumina.⁸ DFT calculations indicate that **2** lies *ca.* 89 kJ mol⁻¹ higher in energy than **1**, and hence is inaccessible under normal thermal conditions. Model calculations on [CH₃ReO₂{(η²-OSiH₂)₂O}] **4**, the product formed by condensation of [CH₃ReO₃] with disilanol ([H₂Si(OH)₂O]), show the tautomeric H-atom transfer to occur preferentially to an Re–O–Si bridging oxygen atom rather than to an Re=O unit. The resulting carbene species [H₂C=ReO₂{(η²-OSiH₂)₂O}(SiH₂OH)] **5** is effectively stabilised by *ca.* 48 kJ mol⁻¹ relative to complex **4**. This alternative H-atom transfer to the Re–O–Si bridge would

seem to be a more realistic mechanism for carbene formation on supported [CH₃ReO₃].

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