is possible that this difference stems from the fact that $Fe(CO)_4$ has a triplet ground state, whereas each of the $M(CO)_5$ molecules of the group 6 metals M almost certainly has a singlet ground state.[21] Attention has already been drawn to the parallel between $Fe(CO)_4$ and an organic carbene (see section 1).[23] Intriguingly, however, experiments aimed at trying to detect a superoxoiron carbonyl derivative resembling the organic carbonyl oxide X, and formed by the *thermal* reaction between $Fe(CO)_4$ and O_2, were to no avail. On the other hand, the first detectable *photo*product A is plainly analogous to the organic dioxirane XI.

(iii) There is no sign of any molecule containing a linear dioxoiron moiety resembling *trans*-$O_2M(CO)_4$ (M = Mo or W).[11] This observation is not totally unexpected, since *trans*-$O_2Cr(CO)_4$ plays, at best, a minor role in the matrix photooxidation of $Cr(CO)_6$. With $Ru(CO)_5$ or $Os(CO)_5$ as the precursor, the picture may be significantly different.

(iv) The first appearance of CO_2 on UV photolysis of the $Fe(CO)_5/O_2$ system seems to be linked to the fate of the intermediate B and its photodissociation to form D, which we believe to be OCFeO. No intermediate analogous to D is observed during the photooxidation of a group 6 hexacarbonyl; indeed, the evolution of CO_2 is not obviously linked to any one stage of the reaction sequence.[11-13]

(v) The $Fe(CO)_5/O_2$ system features an intermediate E which appears to require a second molecule of O_2 for its formation. By contrast, the $M(CO)_6/O_2$ systems (M = Cr, Mo, or W) give rise to no oxometal carbonyl intermediates of this type, and there is no suggestion that a second molecule of O_2 becomes involved until the ultimate stages of the oxidation process are reached, with the formation of binary oxides of the type MO_3 (M = Mo or W) or WO_4 (XXVI).[12,13,18]

With these differences in mind, we will next turn our attention to the binary iron oxide molecules which are produced on prolonged photolysis of O_2-doped argon matrices containing $Fe(CO)_5$.[34] The overall mechanism of the changes will then be reviewed in more detail.

Acknowledgments. We are grateful for support (i) from the SERC for the purchase of equipment and for funding a research assistantship (for M.J.A.) and a studentship (for M.F.) and (ii) from the Northern Ireland Department of Education for funding a studentship (for T.M.G.). We acknowledge with thanks the contributions of Professors M. Poliakoff and J. J. Turner through the computer programs which they kindly made available and through numerous helpful discussions. Studies of the $Fe(CO)_5/O_2$ system under matrix conditions were in fact initiated by this group,[60] including numerous experiments with pure O_2 matrices but none involving isotopic enrichment of either the $Fe(CO)_5$ or the O_2; the experimental results were in line with the ones described here.

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Photooxidation of Matrix-Isolated Iron Pentacarbonyl. 2. Binary Iron Oxide Reaction Products and the Overall Reaction Mechanism

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Received November 27, 1991

Binary iron oxide molecules F and G are generated, together with CO and CO_2, by prolonged UV photolysis (λ = ca. 312 nm) of $Fe(CO)_5$ molecules isolated in O_2-doped argon matrices at ca. 20 K. The identity and likely structure of each of the oxides have been established by analyzing the number, energies, and relative intensities of the IR absorptions displayed by the ^{18}O-enriched molecule in the region 800–1000 cm^{-1}. Hence F is found to be the peroxide $(\eta^2\text{-}O_2)Fe$, in keeping with the conclusions drawn from earlier matrix experiments exploring the interaction of iron atoms with atomic and molecular oxygen. On the other hand, there seems little doubt that the ultimate product G is not O═Fe═O, as suggested previously, but the trioxide FeO_3 with equivalent O atoms and a planar, or near-planar, skeleton conforming to D_{3h} symmetry. This represents the first positive identification of a binary iron(VI) compound. Taken together with the results presented in part 1, the findings point to a more-or-less complete reaction scheme for the matrix photooxidation of $Fe(CO)_5$, as well as inviting comparisons with the details of related oxidation processes.

1. Introduction

In an earlier paper,[2] we presented the background to our investigations of the oxidation reactions induced by the UV photolysis of iron pentacarbonyl in an O_2-doped inert matrix at low temperatures. The IR spectrum of such a matrix witnesses the conversion of the parent carbonyl sequentially (albeit via more than one route) to the oxoiron carbonyl intermediates A–E, with the release of CO and CO_2, ultimately to arrive at two binary iron oxide molecules, F and G. The stoichiometry and likely structure of each of the intermediates A–E we were able to deduce, with varying degrees of confidence, by analysis of the number, energies, and intensity patterns of the IR absorptions associated with the ν(C—O) and ν(O—O) or ν(Fe═O) fundamentals. Here we turn our attention to the final stages of the photooxidation of matrix-isolated iron pentacarbonyl, whereat none of the CO remains coordinated to the metal. We concentrate on the characterization of the products F and G, with the aim of gaining a fuller understanding of the whole reaction scheme set in train by UV irradiation of $Fe(CO)_5/O_2$ mixtures supported in a matrix environment.

2. Experimental Section

The experiments were carried out using the low-temperature apparatus and procedures described elsewhere.[2-6] Matrices were usually prepared by pulsed deposition.[7] IR spectra were recorded with a Perkin-Elmer Model 580A dispersive spectrophotometer affording a resolution and accuracy not exceeding 0.5 cm^{-1}; there was no provision for carrying out

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subtraction routines. Calibration was accomplished by superposition on the recorded spectrum of sharp vibrational/rotational lines due to gaseous HCl, DCl, NH_3, or ND_3.[8]

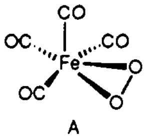
Iron pentacarbonyl (ex Aldrich) was purified by fractional condensation in vacuo, the glass vacuum line being shrouded in aluminum foil to minimize the risk of photodecomposition. Argon, CO, and O_2 were used as supplied by BOC (Research grade); $^{18}O_2$ (98 atom %) was similarly used as supplied by Merck, Sharp and Dohme. Mixtures of the isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ were prepared via the formation and subsequent photodissociation of ^{18}O-enriched ozone, in accordance with the procedure outlined in part 1.[2]

Photolysis experiments made use of either a Philips HPK 125-W or an Oriel 500-W medium-pressure mercury arc. A water filter was employed to minimize the intensity of IR radiation incident upon the matrix during photolysis. In addition, absorption or Balzer's interference filters provided the means of selecting photolyzing radiation confined to a predetermined range of wavelengths.[2]

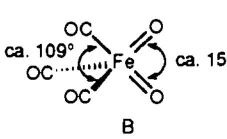
The wavenumbers and relative intensities of the ν(Fe═O) fundamentals in the IR spectrum of an individual iron oxide product FeO_x were calculated at varying levels of ^{18}O enrichment on the basis of a simple energy-factored force field using iterative refinement programs of the type used to perform similar analyses of the ν(C—O) modes of metal carbonyls.[2,9,10] The validity of this approach has been established previously, notably through the matrix studies of Ogden et al.,[11] involving metal oxide derivatives like O_2CrF_2 and O_3OsF_2. IR spectra were then simulated with a program that constructed Lorentzian band shapes of any desired fwhm based on the calculated intensities. The calculations were performed on a VAX computer operated by the Oxford University Computing Service.

3. Results and Discussion

3.1. Overview. When an argon matrix containing $Fe(CO)_5$ and O_2, typically in the proportions $Ar{:}O_2{:}Fe(CO)_5 = 1000{:}50{:}1$ and held at ca. 20 K, was irradiated with ultraviolet light at wavelengths close to 312 nm, the IR spectrum of the matrix witnessed the formation and decay of a number of peroxo- and oxoiron carbonyl molecules (A to E). In an earlier paper[2] we have described how these molecules have been characterized more-or-less certainly by a detailed analysis of their IR spectra, with particular reference to the effects of ^{13}CO and ^{18}O enrichment.



A



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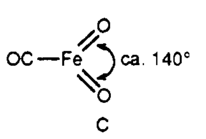

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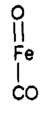

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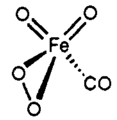

E

Continued photolysis of the same matrix, again with radiation having wavelengths close to 312 nm, resulted ultimately in the extinction of all the infrared absorptions in the region 1950–2200 cm^{-1} associated with coordinated carbonyl groups. This stage was reached after a total photolysis time typically in excess of 8 h, although the precise time varied with the optical properties and also the O_2 concentration of the matrix. The region of the IR spectrum between 800 and 1000 cm^{-1}, associated with ν(O—O) and ν(Fe═O) fundamentals, likewise signaled the elimination of species A to E variously containing (η^2-O_2)Fe, FeO_2, or FeO moieties, as well as coordinated CO groups. At this stage in the photolysis, the spectrum of the matrix displayed, in addition to the usual signs of free CO[12] and CO_2[13] in one form or another, two other absorptions. These occurred at 956 and 945 cm^{-1}, respectively, in the region associated with ν(O—O) or ν(Fe═O) modes. Their response to different conditions of photolysis and annealing left little doubt that they had their origins in *two* different products, which we label F and G, respectively, and which must be presumed to be binary iron oxide molecules.

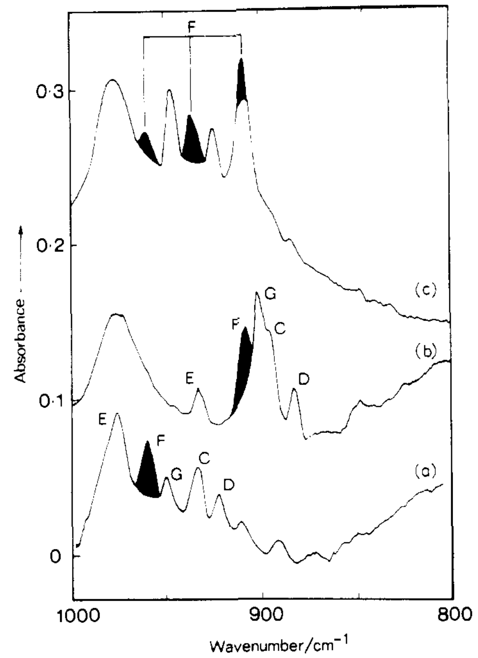

Figure 1. IR spectrum of matrix-isolated F in the region 800–1000 cm^{-1} (product bands marked by black infilling): (a) for a sample generated from $Fe(CO)_5$ and $^{16}O_2$; (b) for a sample generated from $Fe(CO)_5$ and $^{18}O_2$; (c) for a sample generated from $Fe(CO)_5$ and $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the proportions 1:2:1. In each case the matrix had the composition $Ar{:}O_2{:}Fe(CO)_5$ = ca. 1000:50:1 and was maintained at ca. 20 K; photolysis was at λ = ca. 312 nm for 300 min and then at λ = 290–370 nm for 360 min. The broad band centered near 970 cm^{-1} in these and other spectra is associated with an impurity on or in the CsI window.

Continued UV photolysis of the matrix was accompanied by the gradual growth of the band at 945 cm^{-1}, with a concomitant decay of that at 956 cm^{-1}. The findings suggest that the concentration of G increases at the expense of the concentration of F in the matrix. The results of a series of experiments showed that the rate of conversion of F to G depends (i) on the concentration of O_2 in the matrix and (ii) on the temperature of the matrix. Thus, the rate of the reaction was accelerated as the matrix became richer in O_2, the conversion of $Fe(CO)_5$ to G taking ca. 8 h in an argon matrix containing 2% O_2 but only ca. 4 h in an argon matrix containing 10% O_2, but otherwise under similar conditions. In the light of this observation, we propose that a second, or conceivably even a third, molecule of O_2 is implicated in the formation of G. Exploration of the conditions affecting the formation of the photoproducts F and G disclosed too that annealing the matrix to ca. 35 K for 10 min encourages the formation of G at the expense of F.

In this paper we present details of the infrared spectra, including the results of ^{18}O-enrichment studies, which allow us to characterize the molecules F and G and hence to elucidate the overall mechanism governing the matrix photooxidation of iron pentacarbonyl to binary iron oxides in the presence of dioxygen.[2]

3.2. The Binary Iron Oxide F. Associated with the binary oxide F, only one band was observed in the IR spectrum of a photolyzed

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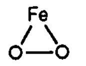
Table I. IR Bands of the Matrix-Isolated Iron Oxide F Observed in the Region 800–1000 cm^{-1}

source	wavenumber (cm^{-1})				asymmetry parameter, ρ[a]
	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	$\Delta(^{16}O_2 - {}^{18}O_2)$	
F[b]	956	932	908	48	1.00
$(\eta^2\text{-}O_2)Fe$[c]	956	931	906	50	1.00

[a] $\rho = 2[\nu(^{16}O_2) - \nu(^{16}O^{18}O)]/[\nu(^{16}O_2) - \nu(^{18}O_2)]$ (see refs 2–5). [b] Generated by UV photolysis (first at λ = ca. 312 nm and then at λ = 290–370 nm) of $Fe(CO)_5$ in an O_2-doped Ar matrix at ca. 20 K. This work; error limits ±2 cm^{-1}. [c] Generated by the interaction of Fe atoms with O_2 molecules in an Ar matrix at 15–40 K. See ref 20.

argon matrix initially containing $Fe(CO)_5$ and $^{16}O_2$. This was centered at 956 cm^{-1}. It shifted to 908 cm^{-1} when $^{18}O_2$ replaced $^{16}O_2$ as the matrix dopant (see Figure 1). The ^{16}O–^{18}O shift of 48 cm^{-1} suggests that F is probably a peroxoiron species.[2,3,14–19]

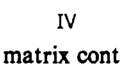
Further evidence supporting this inference comes from experiments involving the UV photolysis of $Fe(CO)_5$ in the presence of a mixture of the isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. These revealed a *symmetrical* triplet of bands centered at 956, 932, and 908 cm^{-1}, and characterized by an asymmetry parameter, ρ, of 1.00.[2–6] Hence the most plausible interpretation is that F is iron(II) peroxide with the triangular structure II.[20]



II

This conclusion is consistent with the results presented by Chang et al.[21] who reported similar frequencies and reached the same structural conclusions as a result of studying the products formed by the cocondensation of iron atoms with dioxygen and an excess of argon. Table I compares the frequencies of the ν(O—O) fundamental for the various isotopomers of $(\eta^2\text{-}O_2)Fe$ (F) generated photolytically from $Fe(CO)_5$ in our experiments with the corresponding results recorded by Chang et al.[21] on the basis of their cocondensation experiments with iron atoms.

3.3. The Binary Iron Oxide G. Prolonged UV photolysis of a $^{16}O_2$-doped argon matrix initially containing $Fe(CO)_5$ generated a binary iron oxide G which was identified with a single IR absorption at 945 cm^{-1}. The wavenumber of this absorption is almost identical with that ascribed with varying degrees of assurance to the matrix-isolated molecule FeO_2 formed either by vaporizing iron from a heated Knudsen cell[22,23] or by sputtering an iron foil[21] and cocondensing the emitted vapors with dioxygen. There is some confusion about the structure of the FeO_2: one view is that it is a peroxo derivative $(\eta^2\text{-}O_2)Fe$,[22] but the more recent verdict favors the bent dioxide structure O=Fe=O (IV).[21,23] However, the results of our experiments utilizing the isotopomers $^{18}O_2$ and $^{16}O^{18}O$, as well as $^{16}O_2$, make it extremely unlikely that G is either $(\eta^2\text{-}O_2)Fe$ or O=Fe=O.



IV

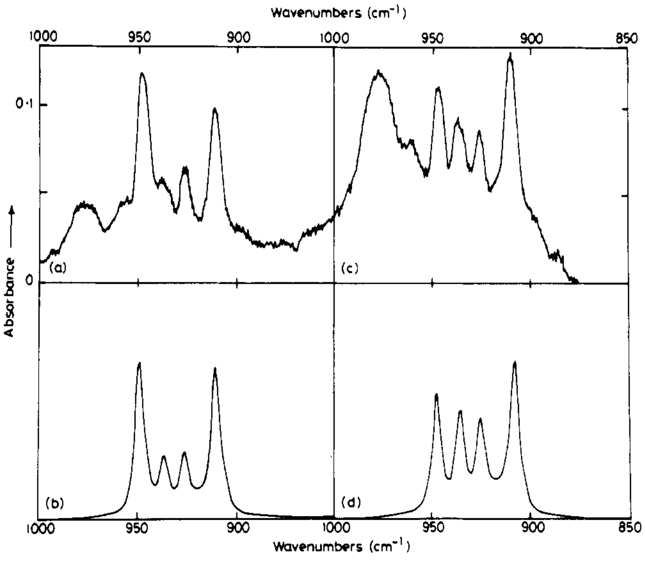


Figure 2. IR spectrum of matrix-isolated G in the region 850–1000 cm^{-1}: (a) spectrum observed for the product generated from $Fe(CO)_5$ and an equimolar mixture of $^{16}O_2$ and $^{18}O_2$; (b) spectrum predicted for ν_3 of a planar FeO_3 molecule with D_{3h} symmetry; (c) spectrum observed for the product generated from $Fe(CO)_5$ and $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the statistical proportions 1:2.5:1.2; (d) spectrum predicted for ν_3 of a planar FeO_3 molecule with D_{3h} symmetry. In each case the matrix had the composition $Ar:O_2:Fe(CO)_5$ = ca. 1000:50:1 and was maintained at ca. 20 K; photolysis was at λ = ca. 312 nm for 300 min and then at λ = 290–370 nm for 360 min. Calculations were based on an energy-factored force field for the ν(Fe=O) modes (see text and Table II).

Table II. Observed and Calculated Wavenumbers for the ν(Fe=O) Modes Associated with the Photoproduct G, Believed To Be FeO_3, Trapped in an Ar Matrix at ca. 20 K

isotopomer	mode	wavenumbers (cm^{-1})				
		observed[a]	calculation A[b]		calculation B[c]	
		$\tilde{\nu}_{obs}$	$\tilde{\nu}_{calc}$	$\tilde{\nu}_{obs} - \tilde{\nu}_{calc}$	$\tilde{\nu}_{calc}$	$\tilde{\nu}_{obs} - \tilde{\nu}_{calc}$
$Fe^{16}O_3$	ν_1 (a$_1'$)	*d*	792.0		792.0	
	ν_3 (e$'$)	945	947.0	−2.0	946.0	−1.0
$Fe^{16}O_2{}^{18}O$	ν_1 (a$_1$)	923	924.5	−1.5	924.3	−1.3
	ν_2 (a$_1$)	*e*	774.4		766.2	
	ν_5 (b$_2$)	945	947.0	−2.0	945.9	−0.9
$Fe^{16}O^{18}O_2$	ν_1 (a$_1$)	935	936.6	−1.6	935.8	−0.8
	ν_2 (a$_1$)	*e*	759.7		751.6	
	ν_5 (b$_2$)	911	909.5	+1.5	910.1	+0.9
$Fe^{18}O_3$	ν_1 (a$_1'$)	*d*	746.7		738.4	
	ν_3 (e$'$)	911	909.5	+1.5	909.9	+1.1

[a] Error limits ±1 cm^{-1}. [b] Based on a planar FeO_3 molecule with D_{3h} symmetry using an energy-factored force field with f_r = 591.3 and f_{rr} = 0 N m^{-1}. [c] Based on a planar FeO_3 molecule with D_{3h} symmetry using a GVFF with ν_4 = 400 cm^{-1}, f_r = 578.3 and f_{rr} = 0 N m^{-1}, and f_α = 1.0 N m rad^{-2}. [d] Infrared inactive. [e] Not observed; expected to be weak.

Photolysis of an argon matrix containing $Fe(CO)_5$, $^{16}O_2$, and $^{18}O_2$, but *not* $^{16}O^{18}O$, reproduced the IR band associated with the all-^{16}O version of G at 945 cm^{-1}, together with a second band associated presumably with the all-^{18}O isotopomer at 911 cm^{-1} (coinciding with the feature ascribed elsewhere[21] to the antisymmetric ν(Fe=O) mode of the molecule $^{18}O=Fe=^{18}O$). In addition, however, the spectrum revealed *two* weaker features due to G; located at 935 and 923 cm^{-1}, these were flanked by the absorptions due to the all-^{16}O and all-^{18}O versions of the molecule (see Figure 2 and Table II). No extra bands were observed when photooxidation of $Fe(CO)_5$ was effected in the presence of a mixture of the dioxygen isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the proportions 1:2.5:1.2. On the other hand, as illustrated in Figure 2, this change in the isotopic composition of the O_2 was seen to cause the two central features (at 935 and 923 cm^{-1}) to gain in intensity with respect to the two outer components of the quartet originating in G. In another experiment, $Fe(CO)_5$ was photooxidized in an argon matrix including $^{16}O_2$ and $^{18}O_2$ in the

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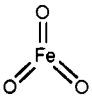
proportions 1:2, again G was characterized by the same four absorptions, but now with the relative intensities I_{945}:I_{935}:I_{923}:I_{911} = 1:0.78:0.44:2.7.

With an energy of 945 cm^{-1} for the ^{16}O parent and a maximum ^{16}O–^{18}O isotopic shift amounting to no more than 34 cm^{-1}, the transition cannot be reconciled either with a ν(O—O) fundamental of a coordinated O_2 group[2,3,14–19] or with the monoxide FeO.[23] By elimination, therefore, we are led to infer that G contains more than one Fe═O bond. Since the ^{16}O–^{18}O shift is also too small for the absorption to be attributed to the t_2 mode of a tetrahedral FeO_4 molecule, only two options seem to remain, namely (i) a dioxide such as II, as suggested previously,[21,23] and (ii) a trioxide FeO_3 possessing either a pyramidal (C_{3v}) or planar (D_{3h}) skeleton. In either case, the absorption must be supposed to represent the antisymmetric ν(Fe═O) mode, and the O═Fe═O bond angle, θ, can be estimated via the equation

$$\sin(\theta/2) \leq \left[\frac{M(m - Rm')}{2mm'(R - 1)}\right]^{1/2}$$

linking θ to $R = \nu_{as}(Fe^{18}O_x)^2/\nu_{as}(Fe^{16}O_x)^2$ and the masses of the metal, M, and ^{16}O and ^{18}O atoms, m and m', respectively. The results suggest an *upper* limit of 180° for θ. Hence it appears that G is either a dioxide, O═Fe═O (IV), with a bond angle approaching 180°, or a trioxide, FeO_3 (XXVIII), which is planar or nearly so. This conclusion is consistent with our failure to find any sign of an IR absorption identifiable with the symmetric ν(Fe═O) mode of G. The limiting value of the ratio $I(\nu_s)/I(\nu_{as})$[25] consistent with the results of our experiments implies a *minimum* O═Fe═O bond angle of ca. 160° for the dioxide II or ca. 117° for the trioxide XXVIII.



XXVIII

The issue of whether G is in fact a dioxide or a trioxide is resolved by the absorption properties displayed by the mixed ^{16}O/^{18}O isotopomer(s) $Fe^{16}O_x{}^{18}O_y$. A dioxide would be expected to show a *single* absorption associated with the molecule ^{16}O═Fe═^{18}O with an energy intermediate between those of ν_{as}(Fe═O) for the symmetrical isotopomers ^{16}O═Fe═^{16}O and ^{18}O═Fe═^{18}O; starting from a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the proportions 1:2.5:1.2 would be expected therefore to give a 1:2.5:1.2 triplet of absorptions with unsymmetrical spacing corresponding to the different versions of FeO_2 (cf. the behavior of the molecule $O_2Fe(CO)_3$[2]). The results we have observed are plainly quite at odds with these expectations and would seem unequivocally to rule out the identification of G as a dioxide, O═Fe═O (IV). Instead we find an isotopic pattern strongly suggestive of a symmetrical metal trioxide, FeO_3 (XXVIII). Qualitative support for this verdict comes from the resemblance of the isotopic pattern to those shown by the relatively well characterized molecules MoO_3,[17] WO_3,[3,5,26] and $FMnO_3$.[27]

The quartet associated with ^{18}O-enriched G has a slight but significant asymmetry which indicates that the IR-silent symmetric ν(Fe═O) fundamental has an energy appreciably *lower* than that of the antisymmetric fundamental, despite the precedent set by WO_3[26] for which the energies are in the reverse order. We have carried out a partial normal coordinate analysis based on a simple energy-factored force field, including intensity calculations,[11,26] with the aim of simulating the ν(Fe═O) region of the IR spectrum due to ^{18}O-enriched G. With the assumption of a planar FeO_3 molecule possessing D_{3h} symmetry and a principal Fe═O stretching force constant, f_r, of 591.3 N m^{-1} and an interaction constant, f_{rr}, set at zero, it was thus possible to reproduce satisfactorily the energies of the observed IR absorptions. Still more persuasive was the way in which the model accounted for the relative intensities on the assumptions that the isotopomers $Fe^{16}O_x{}^{18}O_{3-x}$ were generated in statistical proportions only from a scrambled mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, but that the product derived from $^{16}O_2$ and $^{18}O_2$ in equimolar proportions was made up of $Fe^{16}O_3$, $Fe^{16}O_2{}^{18}O$, $Fe^{16}O^{18}O_2$, and $Fe^{18}O_3$ in the nonstatistical proportions 1:1:1:1. How well the calculations match the experimental results may be gauged by the details shown graphically in Figure 2 and numerically in Table II (calculation A).

There are two aspects which catch the eye.

(i) Such discrepancies as exist between the observed and calculated vibrational energies are only marginally outside the limits of experimental error (having regard to the relatively diffuse nature of the bands) and probably arise from the approximations inherent in the highly simplified force field which we have adopted for the analysis. In fact, there is a bending fundamental, ν_4, with the same irreducible representation (e′) as the antisymmetric ν(Fe═O) mode, ν_3, and the two fundamentals may well couple to an appreciable extent, thereby contravening the basis of the energy-factored force field. An earlier matrix study of the reaction between iron atoms and oxygen[22] led to the identification of a band at 517 cm^{-1}, having a ^{16}O–^{18}O isotopic shift of 13 cm^{-1}, with the species responsible for the band near 945 cm^{-1}. The 517-cm^{-1} band was assigned then to an Fe—O stretching mode of the molecule (η^2-O_2)Fe, although the observed isotopic shift is compatible less with such an assignment than with the bending vibration of an O═Fe═O unit having a bond angle of ca. 120°. Our experiments failed to disclose any absorption hereabouts which could be attributed to G, but this may well be a sign of low concentration, exacerbated by a modest extinction coefficient, more than a cause for doubting the earlier results. Should the bending mode ν_4 of FeO_3 have an energy as high as 517 cm^{-1}—or even, as seems more likely, ca. 400 cm^{-1} [27–29] —an energy-factored force field is unlikely to reproduce exactly the energies of the observed vibrational transitions. Indeed, with the assumption that ν_4 = 400 cm^{-1} for $Fe^{16}O_3$ and that the in-plane bending force constant f_α = 1.0 N m rad^{-2}, a GVFF analysis can be made to reproduce the vibrational energies of G *within* the limits of experimental error (Table II, calculation B). For there to be a realistic prospect of observing ν_4, as well as the out-of-plane bending mode, ν_2 (a_2''), however, the matrix concentration of G will need to be increased, possibly by an order of magnitude, above the present levels (ca. 1:2000).

(ii) On the evidence of experiments with equimolar mixtures of $^{16}O_2$ and $^{18}O_2$, oxidation at iron proceeds initially via *concerted* addition of the O_2 giving only $Fe^{16}O_2$ and $Fe^{18}O_2$ moieties, as in the dioxoiron carbonyl, $O_2Fe(CO)_3$;[2] prolonged photolysis induces oxygen atom transfer so that all four ^{16}O/^{18}O isotopomers of FeO_3 are formed, but in the proportions $Fe^{16}O_3$:$Fe^{16}O_2{}^{18}O$:$Fe^{16}O^{18}O_2$:$Fe^{18}O_3$ = 1:1:1:1. By contrast, experiments starting with a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in statistical proportions afford a mixture of the products $Fe^{16}O_3$, $Fe^{16}O_2{}^{18}O$, $Fe^{16}O^{18}O_2$, and $Fe^{18}O_3$ also with statistical weighting.

It follows, then, that the most plausible interpretation is that G is iron trioxide, FeO_3, probably with a planar structure, XXVIII, rather than a pyramidal one. Despite its d^2 configuration, FeO_3 appears to be isostructural with the d^0 molecules MoO_3[17] and WO_3.[3,5,26] Anionic oxoiron(VI) derivatives, e.g. $M^I{}_2FeO_4$ and $M^{II}FeO_4$ (M^I = alklai metal; M^{II} = alkaline-earth metal), have been known for some years.[30] Prepared typically by the oxidation of a suspension of iron(III) oxide in concentrated alkali, they

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(25) See, for example: Smit, W. M. A. *J. Mol. Struct.* **1973**, *19*, 789. Burdett, J. K.; Poliakoff, M.; Turner, J. J.; Dubost, H. *Adv. Infrared Raman Spectrosc.* **1976**, *2*, 1.

(26) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *89*, 145.

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contain the tetrahedral FeO_4^{2-} anion which is a very powerful oxidizing agent, the standard potential for the aqueous couple FeO_4^{2-}/Fe^{3+} having been estimated to be about +2.0 V at $a_{H^+} = 1$. To the best of our knowledge, the identification of the molecule FeO_3 as one of the ultimate photooxidation products of matrix-isolated $Fe(CO)_5$ represents the first sighting of a binary iron(VI) compound. The results of our experiments illustrate once again the scope of matrix photooxidation of a metal carbonyl for the generation in situ of binary metal oxide molecules.

We cannot of course be certain that our product G, which we judge to be FeO_3, is the same as the absorber identified variously as $(\eta^2\text{-}O_2)Fe$[22] and the bent O=Fe=O species (IV)[21,23] on the basis of earlier matrix experiments involving the oxidation of iron atoms. However, the matching to within 1 cm^{-1} of the IR wavenumbers associated with the all-^{16}O and all-^{18}O isotopomers would seem to provide strong circumstantial evidence that the products are one and the same. Hence it follows that the trapping of iron atoms in an argon matrix including O_2 molecules and O atoms yields among the products FeO_3. This still leaves unanswered a number of questions concerning the earlier experiments. For example, why should FeO_3, as we now identify it, behave as a "metastable" species in an argon matrix including iron atoms, O_2 molecules, and O atoms,[21] and "disappear" when the matrix is annealed to 25 K? We found no such evidence of thermal instability of G at temperatures up to at least 30 K. It would be easier to explain this and other discrepancies if we could be sure of the exact roles played in the earlier experiments by iron clusters Fe_x ($x \geq 2$), O atoms, and other matrix ingredients. Despite the relative complexity of its photooxidation, then, $Fe(CO)_5$ does seem to offer some distinct advantages over iron atoms as a source of binary iron oxides.

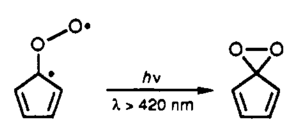
3.4. Overall Reaction Mechanism for the Matrix Photooxidation of $Fe(CO)_5$. Taken in conjunction with the results of the experiments reported in part 1,[2] the findings described here lead us to propose in Scheme I a complete mechanism for the photooxidation of iron pentacarbonyl in an O_2-doped argon matrix, proceeding via oxoiron carbonyl intermediates A–E to the binary iron oxides F and G.

The mechanism includes several features which merit some elaboration.

(i) The peroxoiron tetracarbonyl A is formed by the reaction of the unsaturated primary photoproduct $Fe(CO)_4$[31] with O_2. It appears from our experiments, however, that this reaction does not take place spontaneously when the matrix is annealed at temperatures up to 35 K but requires photochemical activation.

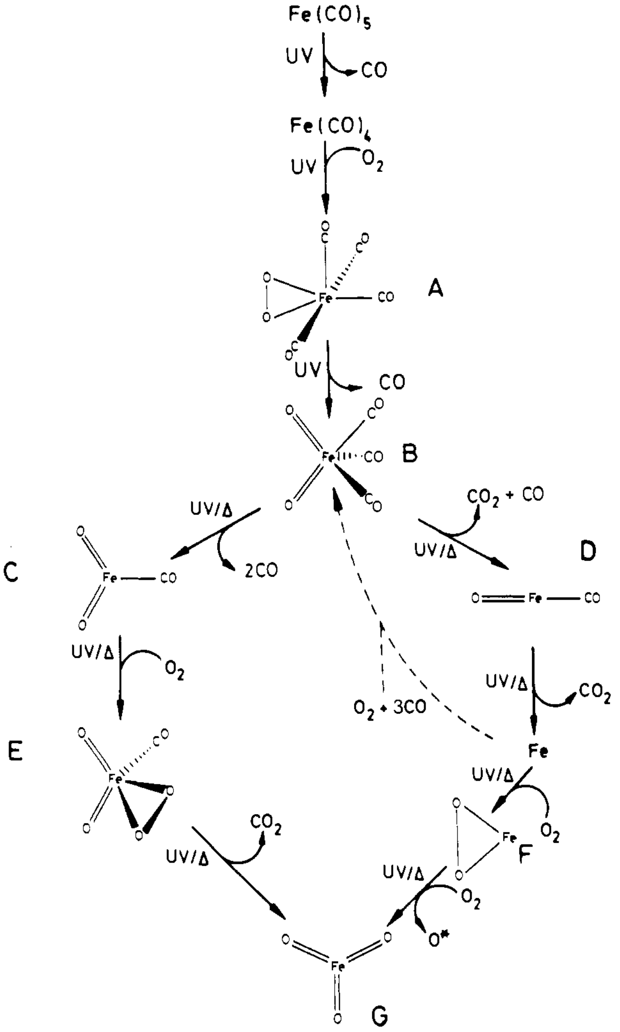
$$Fe(CO)_5 \xrightarrow[-CO]{h\nu\ (\lambda\ =\ ca.\ 312\ nm)} Fe(CO)_4 \xrightarrow[+O_2]{h\nu\ (\lambda\ =\ ca.\ 312\ nm)} \underset{A}{(\eta^2\text{-}O_2)Fe(CO)_4}$$

On the face of it, $Fe(CO)_4$ appears thus to differ from a carbene like cyclopentadienylidene, its isolobal analog, which combines thermally with O_2 in an argon matrix to give what is believed to be a carbonyl oxide (X) in the first instance.[32] On the other hand, A is an obvious analog of the dioxirane XI which derives from the photochemically induced isomerization of X. Although we have failed as yet to detect a superoxo derivative $(\eta^1\text{-}O_2)Fe(CO)_4$ resembling the carbonyl oxide X, and which may be the immediate precursor to A, further experiments along these lines are planned.



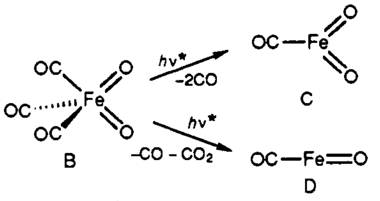
X XI

Scheme I. Photochemistry of the System $Fe(CO)_5/O_2$ in an Ar Matrix at Temperatures near 20 K



(ii) A is itself destroyed by continued photolysis with light having wavelengths near 312 nm, yielding dioxoiron tricarbonyl, B. This process involves the rupture of the O–O bond of the peroxoiron moiety and the loss of one coordinated CO group from A; there is a simultaneous growth of the band near 2140 cm^{-1} due to photoejected CO[12] at this stage. Experiments starting with a mixture of $^{16}O_2$ and $^{18}O_2$, but no $^{16}O^{18}O$, give only the all-^{16}O and all-^{18}O versions of B, with no hint of the "mixed" $^{16}O/^{18}O$ version; hence we infer that the dioxoiron unit of B has its origin in a single O_2 molecule which neither dissociates prior to coordination at the metal center in A nor undergoes scrambling with another O_2 molecule once it is coordinated.

(iii) B may suffer one of two fates on continued UV irradiation. Loss of two molecules of CO yields dioxoiron monocarbonyl, C, while loss of CO and CO_2 yields monoxoiron monocarbonyl, D. Concurrently with the formation of C and D, the absorption due to free CO[12] continues to grow, while that due to free CO_2[13] makes its first appearance. Although we cannot rule out entirely the *sequential* formation of D from C, as these products are at no stage formed in concentrations exceeding ca. 1:10000, the circumstantial evidence of our experiments is that both grow *together* as a result of the photochemical or thermal decay of B.



*λ = ca. 312 nm

(1)

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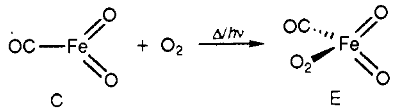
[31] Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276. Poliakoff, M. *Chem. Soc. Rev.* **1978**, *7*, 527. Poliakoff, M.; Weitz, E. *Acc. Chem. Res.* **1987**, *20*, 408.

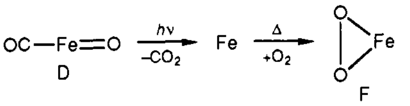
[32] Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154. Bell, G. A.; Dunkin, I. R.; Shields, C. J. *Spectrochim. Acta, Part A* **1985**, *41A*, 1221. Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1842.

(iv) Concentration studies involving argon matrices doped with varying amounts of O_2 (ranging from ca. 2 to 10%)[2] leave little doubt that more than one molecule of dioxygen is involved in the formation of the iron-containing products detected in the later stages of photooxidation. These products include the dioxoiron carbonyl intermediate E (in which the CO is very weakly bound to the metal center) and the binary iron oxides F and G. Thus, E appears to be formed through the uptake of a second molecule of O_2 by the dioxoiron monocarbonyl, C; whether this reaction is photolytically or thermally initiated remains unclear.



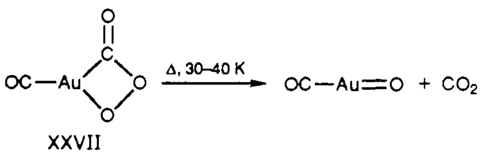
(2)

(v) In the circumstances of our experiments, the most obvious route to iron(II) peroxide, F, involves the intermediacy of "naked" iron atoms, in accordance with eq 3. There is certainly some evidence in favor of this reaction sequence. Firstly, the concentration of free CO_2 in the matrix continues to build up during the conversion of D to F. Secondly, iron atoms have been detected by their optical absorption spectrum on prolonged UV photolysis of $Fe(CO)_5$ trapped alone in an argon matrix;[33a] elemental iron is also one of the ultimate products in the complex photochemistry displayed by $Fe(CO)_5$ adsorbed on porous Vycor glass.[33b] The rate of photodecomposition of $Fe(CO)_5$ we have found to be accelerated appreciably by the introduction of O_2 into an inert matrix. Thus it seems at least plausible that iron atoms are formed in our experiments, but it is equally certain that such atoms would be scavenged by the O_2 to form F, since this reaction is known to be rapid, even at 20 K.[21-23] We have carried out several experiments aimed at measuring the UV–visible absorption spectrum of an O_2-doped argon matrix initially containing $Fe(CO)_5$ to determine its response to prolonged UV photolysis. That none of these experiments produced a hint of any features attributable to atomic iron[33] cannot be found too surprising. In the first place, the scavenging effect of the comparatively large excess of O_2 would be likely to reduce the concentration of free iron atoms in the matrix to a low level. Secondly, those photoproducts of our experiments that we have been able to identify show broad UV–visible absorptions which would be likely to mask any weak absorptions originating in iron atoms at high dilution. Thirdly, the experiments were hampered by the deterioration in the optical properties of the matrix which was an inevitable consequence of long photolysis times (>3 h).



(3)

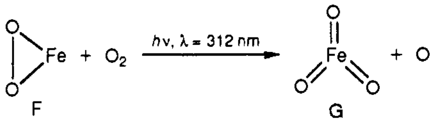
There is at least one precedent for a matrix reaction involving the elimination of CO_2 from an oxometal carbonyl molecule, as in eq 3, that is apart from the implications of similar reactions attending the photooxidation of matrix-isolated $M(CO)_6$ molecules (M = Cr, Mo, or W).[3-5] Ozin and his co-workers have observed loss of CO_2 when the matrix-isolated molecule believed to be gold(II) peroxyformate (XXVII) is warmed to 30–40 K.[34] However, any thought that a product similar to XXVII might be formed through the photooxidation of $Fe(CO)_5$ must be dismissed, for our experiments gave no sign of IR absorption in the neighborhood of 1800 cm^{-1}, one of the distinguishing features of XXVII.



(4)

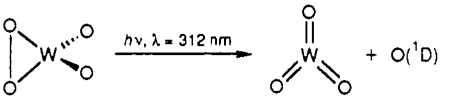
(vi) There are two possible routes to iron(VI) oxide, FeO_3, the molecule which we observe as the ultimate product G in the photooxidation sequence.

I. With the relatively O_2-rich matrices which we used, there are likely to be sufficient O_2 molecules in the proximity of the metal center for the following photolytically activated change to occur, presumably by way of an adduct such as $(\eta^2\text{-}O_2)Fe\cdots O_2$



(5)

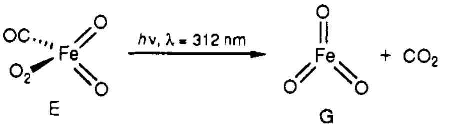
This process finds an obvious echo in the matrix reaction whereby WO_3 is formed from the molecule $(\eta^2\text{-}O_2)WO_2$[3,5]



(6)

On the evidence of trapping experiments involving the introduction of N_2 or CH_4 into the matrix, the oxygen atoms produced with the WO_3 are presumed to be in the excited ^1D electronic state.[5] It seems likely therefore that the oxygen atoms released with the conversion of F to G are also in their ^1D state. In this case there is the possibility of secondary reactions between the excited O atoms and CO, CO_2, $(\eta^2\text{-}O_2)Fe$ (F), and O_2 to generate CO_2,[35] CO_3,[36] FeO_3, and O_3,[37] respectively. We saw no spectroscopic evidence suggesting the formation of either O_3 or CO_3 in any of our experiments. However, both of these molecules are photolabile at wavelengths close to 312 nm, and so, if formed, they would be subject to the attainment of a photostationary state in which their steady-state concentrations could well be undetectably small under the conditions of our experiments.

II. A second route to G is by elimination of CO_2 from E (eq 7), a process which also bears a resemblance to reaction 4 above.[34]



(7)

In practice, it is probable that both these reactions occur, with route I predominating at higher O_2 concentrations, thus accounting for an increase in the rate of FeO_3 production disproportionately greater than the enhanced build-up of E would lead us to expect. Consideration of the two mechanisms also provides an explanation of how the isotopomers $Fe^{16}O_2{}^{18}O$ and $Fe^{16}O^{18}O_2$ come to be produced, even in matrices containing initially only the symmetrical dioxygen isotopomers $^{16}O_2$ and $^{18}O_2$. Thus, $Fe^{16}O_2{}^{18}O$ and $Fe^{16}O^{18}O_2$ may be formed from the appropriate isotopic versions of E and F by mechanisms I and II. If the matrix contains initially equimolar proportions of $^{16}O_2$ and $^{18}O_2$, both mechanisms would therefore be expected to lead to the isotopomers $Fe^{16}O_3$, $Fe^{16}O_2{}^{18}O$, $Fe^{16}O^{18}O_2$, and $Fe^{18}O_3$, but in the nonstatistical proportions 1:1:1:1; implicit in our arguments are the assumptions (a) that the O atom displaced derives *exclusively* from a coordinated O_2 unit (in the form of either a peroxo- or a dioxoiron moiety), and (b) that mechanism I does not permit scrambling of O_2 molecules at a rate approaching that of O atom displacement. As indicated by the portions of the spectra reproduced in Figure 2, our experiments give results pleasingly consistent with these proposals.

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Mechanism I

$$\left.\begin{array}{l}(\eta^2\text{-}^{16}O_2)Fe + {}^{18}O_2 \xrightarrow{h\nu} Fe^{16}O^{18}O_2 + {}^{16}O \\ (\eta^2\text{-}^{18}O_2)Fe + {}^{16}O_2 \xrightarrow{h\nu} Fe^{16}O_2{}^{18}O + {}^{18}O \\ \quad F \qquad\qquad\qquad\qquad\quad G\end{array}\right\} \quad (8)$$

Mechanism II

$$\left.\begin{array}{l}(\eta^2\text{-}^{16}O_2)^{18}O_2FeCO \xrightarrow{h\nu} Fe^{16}O_2{}^{18}O + {}^{18}OC^{16}O \\ (\eta^2\text{-}^{18}O_2)^{16}O_2FeCO \xrightarrow{h\nu} Fe^{16}O^{18}O_2 + {}^{16}OC^{18}O \\ \quad E \qquad\qquad\qquad\qquad\quad G\end{array}\right\} \quad (9)$$

4. Conclusions

Our experiments provide persuasive spectroscopic evidence that two binary iron oxides are generated by prolonged UV photolysis of iron pentacarbonyl trapped in an O_2-doped argon matrix. The products in question are $(\eta^2\text{-}O_2)Fe$ and FeO_3 with the structures II and XXVIII, respectively. Hence we have been able to complete our analysis of the steps which take place as photooxidation proceeds, via a variety of oxoiron carbonyl intermediates (A–E), first to $(\eta^2\text{-}O_2)Fe$ and ultimately to FeO_3, while all the CO originally coordinated to the metal center is converted in the end to CO_2. Scheme I presents a mechanism which takes account of all the photoproducts reported in parts 1[2] and 2 of this investigation.

The results reported here, relating to the final stages of the photooxidation of iron pentacarbonyl, invite obvious comparisons with earlier experiments in which iron atoms were cocondensed with oxygen or oxygen/argon mixtures.[21-23] The earlier studies brought to light IR absorptions with wavenumbers virtually identical to those we assign to the absorbers $(\eta^2\text{-}O_2)Fe$ and FeO_3, but the spectra were interpreted rather differently. Certainly our results are consistent with, and lend support to, the earlier characterization of the peroxide $(\eta^2\text{-}O_2)Fe$.[21] On the other hand, our analysis must cast some doubt on the identification of FeO_2[21-23] as the source of the absorption near 945 cm^{-1}.

It is of interest to compare the binary metal oxides produced by the matrix photooxidation of different metal carbonyls, viz. $Fe(CO)_5$, $Cr(CO)_6$,[6] $Mo(CO)_6$,[5] $W(CO)_6$,[5] and $Mn_2(CO)_{10}$.[38] The group 6 carbonyls show a progressive trend in which the +6 oxidation state seems to be more readily attained in the sequence Cr < Mo < W. Thus, $Cr(CO)_6$ yields CrO_2 as the ultimate oxidation product,[6] whereas $Mo(CO)_6$ gives a mixture of MoO_2 and MoO_3, with MoO_2 being converted gradually to MoO_3 on prolonged broad-band irradiation.[5] By contrast, the photooxidation of $W(CO)_6$ gives no vestige of WO_2, except in the coordinated form of derivatives like $O_2W(CO)_n$ (n = 2 or 4);[3-5] instead WO_3 is the final product, and this in turn evolves from another tungsten(VI) derivative $(\eta^2\text{-}O_2)WO_2$. In view of the behavior of $Cr(CO)_6$, it may come as a surprise that $Mn_2(CO)_{10}$ is oxidized ultimately to Mn_2O_7.[38] However, thermodynamic considerations are by no means the only factor determining the nature of the ultimate products in these reactions. Because the experiments entail long periods of broad-band photolysis, the outcome is likely to hinge on the photolability of the different products, notably in relation to the characteristics of the photolyzing radiation. Thus, the apparent stability of FeO_3, under conditions which will not support CrO_3,[6] may well reflect a fortuitous lack of coincidence between its optical absorption properties and the principal regions of emission of the photolysis sources used in our experiments.

The detection of FeO_3 raises also the teasing question of whether the iron analog of the tetraoxides RuO_4 and OsO_4 might also be amenable to matrix synthesis. Recent reports claim that this compound can in fact be generated either by disproportionation of ferrate(VI) or by electrochemical means.[39] With the incorporation into a solid cryogenic matrix of an oxidant more powerful and photolabile than dioxygen, e.g. O_3, and the adoption of more selective conditions of photolysis, it may be feasible to devise alternative access to FeO_4.

Acknowledgments. We thank the SERC for supporting this research and for funding a research assistantship (for M.J.A.) and a studentship (for M.F.). We also acknowledge with gratitude the contributions of Professors M. Poliakoff and J. J. Turner through the computer programs which they kindly made available and through numerous stimulating discussions.

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Notes

Contribution from the Dipartimento di Chimica,
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Irreversible Addition of Arenediazonium Ligands to a Pt–Pt Bond. Solid-State Structure of $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)]BF_4$

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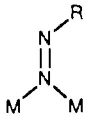
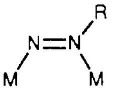
Introduction

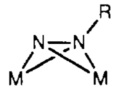
The chemistry of arenediazonium complexes has attracted a great deal of attention,[1] but only a small fraction of studies involves coordination of the arenediazenido (ArN_2) ligand to dinuclear complexes in a bridging position. Four different structural types (I–IV) have been characterized.[2]



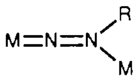
I



II



III



IV

Although the reactivity of diazonium salts with several metal derivatives containing dppm (dppm = $Ph_2PCH_2PPh_2$) as a bridging ligand has been previously reported,[3-6] the only structural

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(1) (a) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, p 130. (b) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443.

(2) See, for example: (a) Einstein, F. W. B.; Yan, X.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1990**, 1446. (b) Bruce, M. I.; Williams, M. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1986**, *309*, 157. (c) Samkoff, D. E.; Shapley, J. R.; Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1984**, *23*, 397. (d) Hillhouse, G. L.; Haymore, B. L.; Bistram, S. A.; Herrmann, W. A. *Inorg. Chem.* **1983**, *22*, 314. (e) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1983**, *22*, 1214. (f) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1580.

(3) Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978**, *27*, L85.

(4) Woodcock, C.; Eisenberg, R. *Organometallics* **1985**, *4*, 4.

(5) Uson, R.; Fornies, J.; Espinet, P.; Fortuno, C. J. *Chem. Soc., Dalton Trans.* **1986**, 1849.

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