Infra-red Lasers: a New Tool for Studying the Diazotization of Matrix Isolated Tetracarbonyliron(0)

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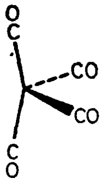
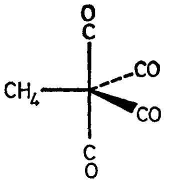
Summary For both i.r. laser and broad band near-i.r. irradiation of $[Fe(CO)_4]$ in a nitrogen matrix at 20 K, the quantum yield for intramolecular isomerization is considerably greater than the quantum yield for reaction with N_2.

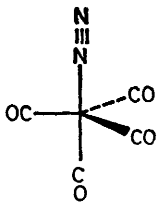
We have previously demonstrated[1] that i.r. lasers can provide valuable evidence about the photochemistry of matrix-isolated $[Fe(CO)_4]$, produced by u.v. photolysis[2,3] of $[Fe(CO)_5]$ at 20 K. Matrix-isolated $[Fe(CO)_4]$ has a C_{2v} structure‡ (**1**). When isotopically enriched $[Fe(^{12}C^{16}O)_{4\text{-}x}\text{-}{}^{13}C^{18}O)_x]$, isolated in an argon matrix, is irradiated with a continuous-wave CO laser [*i.e.* absorption by ν(C–O) modes] the molecule undergoes intramolecular exchange of CO ligands between 'axial' and 'equatorial' positions, producing a non-statistical distribution of $^{13}C^{18}O$ groups.[4] Subsequent exposure to near-i.r. radiation (9000—13,000 cm^{-1}) also promotes ligand exchange[4] and restores the statistical distribution of $^{13}C^{18}O$. In a methane matrix, the laser causes the fast reaction of $[Fe(CO)_4]$ with CH_4, to form a $[CH_4Fe(CO)_4]$ complex, (**2**); in methane no rearrangement without reaction can be detected.[1]



(1)



(2)



(3)

We have performed experiments in a nitrogen matrix, where $[Fe(CO)_4]$ could either rearrange, as in argon, or react with the matrix, as in methane, to form an $[Fe(CO)_4N_2]$ complex (**3**). The results of the experiments are shown in

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‡ The structures (**1**), (**2**) and (**3**) were deduced from i.r. spectra; see ref. 2.

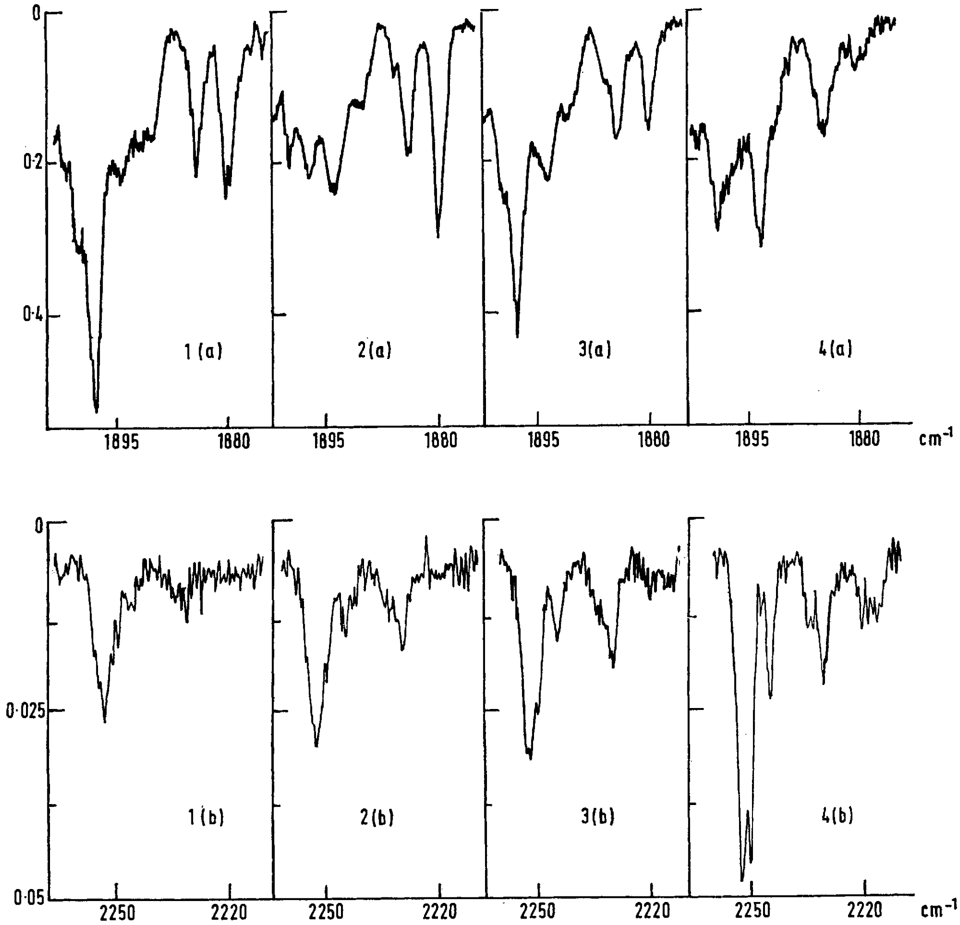

FIGURE. Part of the i.r. spectrum (in absorbance) of an N_2 matrix§ originally containing $[Fe(CO)_5]$ enriched with *ca.* 65% $^{13}C^{18}O$, showing (a) 'C–O' (1900—1875 cm^{-1}) and (b) 'N–N' stretching regions (2260—2210 cm^{-1}); $[Fe(CO)_5]:N_2$ 1:3000. (1) After u.v. photolysis with Hg arc to generate $[Fe(CO)_4]$; (2) after 3 min irradiation with the c.w. CO laser, 700 mW at 1897·6 cm^{-1}, co-incident with the strongest band in (1a);¶ (3) after 2·5 min exposure to the unfiltered spectrometer source (near-i.r. radiation); (4) after a further 15 min near-i.r. radiation; all CO-stretching bands are now due to $[Fe(CO)_4N_2]$. All spectra were recorded with a coated Ge filter (OCLI) at the pre-sample common beam focus of a Perkin-Elmer 580 spectrophotometer, and with *ca.* 1 cm^{-1} slitwidth. Note the expanded ordinate and contracted abscissa scale of the lower spectra, which were recorded with slightly lower resolution.

the Figure. U.v. photolysis of $[Fe(CO)_5]$ in a nitrogen matrix[3] produces largely $[Fe(CO)_4]$. The bands in spectrum 1(a) (Figure) are, therefore, assigned to different isomers of $[Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x]$ and the weak band in the N–N stretching region in spectrum 1(b) is due to a small quantity of $[Fe(CO)_4N_2]$ produced during u.v. photolysis. The following conclusions can be drawn from the experiment.

(i) Laser irradiation in the C–O stretching bands of $[Fe(CO)_4]$ produces only a small change in the N–N stretching region of the spectrum [compare spectra 2(b) and 1(b)]. In the C–O stretching region, however, there is a striking decrease in the intensity of the irradiated band, and growth of bands due to other isomers of $[Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x]$ [compare spectra 2(a) and 1(a)]. Similar behaviour was observed on using different lines of the CO laser to irradiate bands at 1894, 1884, and 1881 cm^{-1} (not illustrated). Thus the laser irradiation causes isomerization of $[Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x]$ with little production of $[Fe(CO)_4N_2]$.

(ii) *Brief* exposure to near-i.r. radiation almost restored the original intensity pattern of bands in the C–O stretching region [compare spectra 3(a) and 1(a)], again with only a small change in the N–N stretching region [compare spectra 3(b) and 2(b)]. The near-i.r. radiation has essentially reversed the effect of the laser. Thus, as in argon matrices, the near-i.r. radiation is causing isomerization of $[Fe(CO)_4]$.

(iii) *Longer* exposure to near-i.r. radiation causes a substantial increase in intensity of the N–N stretching band of $[Fe(CO)_4N_2]$ (**3**) [compare spectra 4(b) and 3(b)] and completely changes the C-O stretching region** [compare spectra 4(a) and 3(a)].

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§ Using an Air Products CS-202 Displex cooler at 20 K, CsBr substrate, pulsed matrix deposition, an Edinburgh Instruments PL3 c.w. CO laser and Phillips HPK 125 W medium pressure Hg lamp.

¶ The laser output at this wavelength consists of two closely spaced lines, 1897·6546 and 1897·6199 cm^{-1}, each with a linewidth $<10^{-3}$ cm^{-1}. Similar multiline output occurs at the other wavelengths used for photochemistry.[4]

** There appears to be little change between spectra 3(a) and 4(a) in the region of *ca.* 1884 cm^{-1} because there is a band of $[Fe(CO)_4N_2]$ at 1884·5 cm^{-1}, which is very close to an absorption of $[Fe(CO)_4]$ at 1884·0 cm^{-1}.

Thus, in the nitrogen matrix, for both i.r. laser and broad-band near-i.r. irradiation, the quantum yield for intramolecular isomerization is considerably greater than that for reaction with N_2. Since, however, no isomerization of $[Fe(CO)_4]$ was observed in a methane matrix, the quantum yield for isomerization in methane must be much less than that for reaction with CH_4. Differences in photochemistry between matrices are not unprecedented.[5–7] For example, the i.r. induced *cis* $\rightleftharpoons$ *trans* isomerization of HONO occurred in nitrogen but not in argon matrices.[5] In the present experiment, however, the result is most unexpected, since N_2 is certainly a stronger ligand than CH_4 and intuitively it would be expected to react with $[Fe(CO)_4]$ faster. The observed reaction rates may be due to subtle differences in energy transfer between $[Fe(CO)_4]$ and the two matrices but unfortunately almost nothing is known about energy transfer in matrix-isolated molecules of this size. The only obvious difference between the two matrices lies in the structure of the complexes (**2**) and (**3**). Thus, the addition of CH_4 to the C_{2v} $[Fe(CO)_4]$ fragment (**1**) requires less change in the structure of the $[Fe(CO)_4]$ unit than does the formation of the trigonal $[Fe(CO)_4N_2]$ complex, (**3**). Whatever the correct explanation for these differences, the experiment clearly demonstrates how i.r. lasers provide new information about photochemical reactions in matrices.

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