# INFRARED MULTIPLE-PHOTON DECOMPOSITION OF $Fe(CO)_5$ INDUCED BY AN INFRARED $p-H_2$ RAMAN LASER

Tetsuro MAJIMA, Hideo TASHIRO, Katsumi MIDORIKAWA and Michio TAKAMI

The Institute of Physical and Chemical Research, Hirosawa, Wako-shi. Saitamu 351-01, Japan

Received 1 July 1985

Infrared multiple-photon decomposition (IRMPD) of  $Fe(CO)_5$  induced by an IR  $p-H_2$  Raman laser has been studied. The decomposition efficiently occurs with the irradiation of unfocused laser beam at 616.2 cm<sup>-1</sup>. The decomposition products are mainly CO and metallic iron. In IRMPD of a mixture of  $Fe(CO)_5$  and 1-butene or 1-pentene, isomerization of these olefins by active intermediates is not observed. The results are explained by fast sequential decarbonylation of  $Fe(CO)_5$  in highly excited vibrational states.

#### 1. Introduction

The photochemistry and photophysics of unsubstituted transition metal carbonyls,  $M(CO)_n$ , are of current interest with regard to photocatalytic reactions [1]. Most of the studies on  $M(CO)_n$  were carried out by UV and visible light excitation to electronically excited states. The primary process of decomposition was interpreted to be scission of a single M-CO bond, which generated the reactive intermediate  $M(CO)_{n-1}$ . However, recent spectroscopic studies in the visible and UV region provided evidence of the formation of highly unsaturated species and bare central metal atoms through the loss of several carbonyl ligands as the primary pathway when gas-phase  $M(CO)_n$  was photolyzed with high-energy pulsed lasers [2].

In contrast to many photochemical studies in the visible and UV region, IR photochemistry on  $M(CO)_n$  has received less attention because  $M(CO)_n$  has no absorption bands in the vicinity of the  $CO_2$  laser lines.  $CO_2$  lasers were used to decompose  $M(CO)_n$  by IR photosensitized reaction [3–5] and by dielectric breakdown [6]. Recently infrared multiple-photon decomposition (IRMPD) of  $M(CO)_n$  (M = Ni, Fe, Cr, Mo, and W) has been studied using a frequency-doubled TEA  $CO_2$  laser [7]. Strong 5  $\mu$ m absorption bands of  $M(CO)_n$  were excited with a focused laser beam of several mJ output energy from the laser.

0 009-2614/85/\$ 03.30 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division)

In addition to the 5  $\mu$ m C–O stretching bands, M(CO)<sub>n</sub> has strong IR absorption bands at 16–17  $\mu$ m due to MCO bending vibrations [8]. We have studied IRMPD of Fe(CO)<sub>5</sub> via excitation of the  $\nu_7$  mode at 619.9 cm<sup>-1</sup> with a p-H<sub>2</sub> Raman laser which provides a tunable output energy up to 1.7 J pulse<sup>-1</sup> in the 14–17  $\mu$ m region [9]. The large output power allows us to decompose Fe(CO)<sub>5</sub> with an unfocused (parallel) laser beam. The results are compared with those in IRMPD of Fe(CO)<sub>5</sub> at 5  $\mu$ m with regard to the difference of the excited vibrational modes. In order to study the decomposition mechanism and the catalytic activities of the intermediates, the effects of additive gases such as CO, 1-butene, 1-pentene, and 1,3-butadiene are also examined.

### Experimental

The experimental arrangement is shown in fig. 1. The 10  $\mu$ m R(18), R(12), and R(10) lines of the CO<sub>2</sub> TEA laser (974.62, 970.55, and 969.14 cm<sup>-1</sup>) were shifted to 620.3, 616.2 and 614.8 cm<sup>-1</sup>, respectively, by stimulated rotational Raman scattering in p-H<sub>2</sub> [9, 10]. The p-H<sub>2</sub> Raman laser provided a pulsed laser beam with a width of  $\approx$ 50 ns fwhm and an energy of up to 0.5 J pulse<sup>-1</sup> with a repetition rate of 0.4–1 Hz. A change of the repetition rate had no influence on



Fig. 1. Schematic diagram of the experimental arrangement. TEA, TEA CO<sub>2</sub> laser oscillator; AMP, two-stage TEA CO<sub>2</sub> lasers as amplifiers, M<sub>1</sub>, copper mirror with  $R = \infty$ ; H<sub>2</sub>, p-H<sub>2</sub> Raman cell (400 Torr of p-H<sub>2</sub> at 110 K); M<sub>2</sub>, copper mirror with R = 5 m; M<sub>3</sub>, LiF mirror with  $R = \infty$  for cutting off 10  $\mu$ m CO<sub>2</sub> laser light; A, aperture with a diameter of 1.0 cm; D, polyethylene disks for attenuating laser energy; W, KBr window; C, reaction cell with an irradiation length of 10 cm; IR, IR spectrophotometer; P, joulemeter; N<sub>2</sub>, liquid-nitrogen bath; T, Toepler pump; GC, gas chromatograph; Q-MS, quadrupole mass spectrometer.

the decomposition. A parallel laser beam passed through an aperture of 1.0 cm in diameter, was attenuated by polyethylene disks, and was then introduced into a cross-type Pyrex reaction cell (2.0 cm in diameter, 10 cm in irradiation length, 5 cm in path length for IR analysis, 50 cm<sup>3</sup> in internal volume ( $V_{cell}$ ), and 7.9 cm<sup>3</sup> in irradiated volume ( $V_{irr}$ )). The cell was equipped with KBr windows at four ends and attached to an IR spectrophotometer (JASCO A-102 spectrometer) for IR analysis. The energy of the laser pulses at the entrance window was measured with a Gentec joulemeter.

The partial pressure of Fe(CO)<sub>5</sub> was estimated from the IR absorption peaks at 2000, 645, and 620 cm<sup>-1</sup> before, during, and after the irradiation at room temperature. After the irradiation, carbon monoxide (CO) was separated from the condensable gas at -196°C by means of a Toepler pump and analyzed with a Shimadzu GC-7A gas chromatograph (column, 3 mm X 3 m Unibeads C 60/80; column temperature, 40°C; detector, thermal conductivity cell), and then introduced to a NEVA TE-150 quadrupole mass spectrometer. The condensable gas at -196°C and the solid in the cell were analyzed with the IR spectrophotometer, the mass spectrometer, and a Hitachi 330 UV spectrophotometer. When hydrocarbons were used as additive gas, they were separated from the iron carbonyls by passing through a trap cooled to -20 to -30°C and analyzed with a Hitachi 163 gas chromatograph (column,  $3 \text{ mm} \times 10 \text{ m} 10\%$  Sebaconitrile-Uniport 60/80; column temperature,  $30^{\circ}$ C; detector, flame ionization).

Fe (CO)<sub>5</sub> was purchased from Strem Chemicals Co., purified by vacuum distillation, and degassed by rigorous freeze-pump-thawing just before the irradiation. The pressure of Fe(CO)<sub>5</sub> was measured with a MKS Baratron 221AHS. Other gases were purchased from Takachiho Trading Co. and used after vacuum distillation.

## 3. Results and discussion

Fe(CO)<sub>5</sub> has a strong absorption band at 619.9  $cm^{-1}(\nu_7)$  with an absorption coefficient of 1.81 X  $10^{-2}$  Torr<sup>-1</sup> cm<sup>-1</sup>. The irradiation of Fe(CO)<sub>5</sub> (pressure, 0.5-3.0 Torr) with the parallel laser beam at 614.8, 616.2, or 620.3 cm<sup>-1</sup> (laser fluence, 0.01–0.2  $J \text{ cm}^{-2}$ ) induced highly efficient IRMPD. The decomposition products were CO and metallic iron. The decomposition efficiency slightly increased from 620.3 to 614.8 cm<sup>-1</sup>. Most of the experiments were carried out with the 616.2 cm<sup>-1</sup> laser line, where fluctuation of the pulse energy was relatively small (±10%). Deposition of metallic iron on both the entrance window and the cell wall was observed after irradiation of approximately 100 pulses. No other products were detected by IR spectroscopic, gas chromatographic, and mass spectrometric analyses. The ratio of CO to consumed Fe(CO)<sub>5</sub> was almost constant, [CO]/[consumed  $Fe(CO)_5$ ] =  $P_{CO}/\Delta P_{Fe}$  = 5.0 ± 0.8, and was independent of laser line, laser fluence, pulse number (10-100), conversion (2-30%), and pressure of Fe(CO)<sub>5</sub> (0.3-2 Torr). This ratio is in good agreement with that expected from the stoichiometry of the decomposition:  $Fe(CO)_5 \rightarrow Fe + 5CO$ . The amount of stable unsubstituted iron carbonyls such as  $Fe_2(CO)_9$  and  $Fe_3(CO)_{12}$  was negligibly small.

A plot of  $-\ln(1-X)$  versus pulse number gives a straight line at low conversion as shown in fig. 2, where  $X = [\text{consumed Fe}(\text{CO})_5]/[\text{initial Fe}(\text{CO})_5]$ . According to the first-order decomposition kinetics, the rate constant  $(k_d)$  is determined to be  $k_d = 4.0 \times 10^{-2} \text{ pulse}^{-1}$  from the slope of the linear plots of  $-\ln(1-X)$  versus pulse number. The decomposition probability  $(P_d)$  was given from  $P_d = k_d V_{\text{cell}}/V_{\text{irr}}$ . The fluence dependence of  $P_d$  at 0.5 Torr of Fe (CO)<sub>5</sub>



Fig. 2. Plots of  $-\ln(1 - X)$  versus pulse number, where  $X = [Fe(CO)_5]/[initial Fe(CO)_5]$ . Laser wavenumber, 616.2 cm<sup>-1</sup>; laser energy, 0.12 J pulse<sup>-1</sup>; initial [Fe(CO)<sub>5</sub>], 0.50 Torr.

is shown in fig. 3.  $P_d$  increased with the increase of fluence (F), following to  $P_d \simeq F^{1.8}$ . The decomposition was observed even at a laser fluence of 0.01 J cm<sup>-2</sup>. The extrapolation of the linear plot to  $P_d = 1$ gives  $F_{P_d=1} \approx 0.5 \text{ J} \text{ cm}^{-2}$ , which means that 0.5 Torr of Fe (CO)<sub>5</sub> decomposes in 100% yield by irradiation of one laser pulse with  $F > 0.5 \text{ J} \text{ cm}^{-2}$ . The low  $F_{P_d=1}$ may be due to a high vibrational density of states in the low-energy region and the low value of the average Fe-C bond dissociation energy of 27.7 kcal mol<sup>-1</sup> for Fe(CO)<sub>5</sub> [11]. This average dissociation energy implies the thermodynamic requirement of 75 photons at 16  $\mu$ m per molecule to induce the decomposition Fe(CO)<sub>5</sub>  $\Rightarrow$  Fe + 5CO.



Au et al. have reported  $F_{Pd=1} = 0.032 \text{ J cm}^{-2}$  in IRMPD of 0.35 Torr of Fe(CO)<sub>5</sub> using a focused laser beam at 2012 cm<sup>-1</sup> [7]. This value is about 1/16 of  $F_{Pd=1}$  at 616 cm<sup>-1</sup>. This ratio agrees incidentally with the ratio of 1  $\leftarrow$  0 absorption coefficients at 2000 and 620 cm<sup>-1</sup> due to  $\nu$ (CO) and  $\delta$  (FeCO) of Fe(CO)<sub>5</sub>, respectively [8] ( $\epsilon_{620}/\epsilon_{2000} = 1/17$ ). This result suggests that the decomposition probability is proportional to the linear absorption coefficients of the bands.

In order to study the reactivity of the intermediates produced by IRMPD, effect of additive gases such as CO, 1-butene, 1-pentene, and 1,3-butadiene, of which absorptions were negligibly small at 616 cm<sup>-1</sup>, was examined in detail.  $k_d$  and  $P_d$  decreased with the pressure of additive gases (0-10 Torr) at 0.5 Torr of Fe(CO)<sub>5</sub>. As an example, the effect of CO pressure on  $P_{\rm d}$  is shown in fig. 4. Products were always CO and metallic iron. Thus, these additives acted as quenchers of IRMPD of Fe(CO)<sub>5</sub> at 16  $\mu$ m. The convex curve at high conversions in fig. 2 is also due to the quenching by CO produced in IRMPD of  $Fe(CO)_5$ . The quenching efficiency of a bidentate ligand, 1,3-butadiene, is more than 10 times as much as those of monodentate ligands such as CO, 1-butene, and 1-pentene as shown in table 1. This suggests that the quenching process is not a simple collisional process but involves transient coordination processes of the ligands to vibrationally excited Fe(CO)<sub>5</sub> and to the coordinatively unsaturated intermediates formed in the decomposition. If the coordinatively unsaturated intermediates were produced with the same lifetime as in thermolyses and UV photolyses of  $Fe(CO)_5$ -olefin or -diene mixture, they would usually catalyze several kinds of reactions of



Fig. 3. Dependence of decomposition probability  $(P_d)$  on laser fluence (F). Laser wavenumber, 616.2 cm<sup>-1</sup>; [Fe(CO)<sub>5</sub>], 0.50  $\pm$  0.03 Torr.

Fig. 4. Dependence of decomposition probability  $(P_d)$  on CO pressure. Laser wavenumber, 616.2 cm<sup>-1</sup>; laser energy, 0.090  $\pm$  0.010 J pulse<sup>-1</sup>; [Fe (CO)<sub>5</sub>], 0.50  $\pm$  0.03 Torr.

Table 1	_
Quenching efficiency ( $Q$ ) o	f additive gas <sup>a)</sup>

Additive gas	Q
co	3.6
1-butene	2.5
1-pentene	1.5
1,3-butadiene	37 ± 5

a) Q in Torr<sup>-1</sup> is the slope of linear plots of  $k_d/k_d^A$  versus pressure of additive gas (0.5–10 Torr), where  $k_d$  and  $k_d^A$ are the decomposition rate constants in the absence and presence of additive gas, respectively. Laser wavenumber, 616.2 cm<sup>-1</sup>; laser energy, 0.09 ± 0.03 J pulse<sup>-1</sup>; [Fe (CO)<sub>5</sub>], 0.5 Torr.

olefins such as cis-trans isomerization, 1,3-hydrogen transfer, and hydrogenation in the presence of hydrogen, and/or react with olefins or dienes to form stable olefin- or diene-iron carbonyl complexes [1]. However, neither the isomers of olefins nor the complexes were detected in the present work. Moreover, butane or pentane was not formed in IRMPD of Fe(CO)<sub>5</sub>-1butene or -1-pentene mixture in the presence of hydrogen, where [Fe(CO)<sub>5</sub>] = 0.5, [1-butene or 1-pentene] = 5.0, and [hydrogen] = 10 Torr. Therefore the coordinatively unsaturated intermediates have a lifetime too short to catalyze the isomerization and hydrogenation reactions of olefins and/or to react with olefins or dienes.

The experimental data are consistent with the decomposition mechanism involving sequential decarbonylation of  $Fe(CO)_5^*$  (the asterisk denotes vibrational excitation) [7]. The initial reaction process is the decarbonylation into CO and  $Fe(CO)_4^*$ .  $Fe(CO)_5^*$  has an internal energy larger than required for cleavage of a Fe–C bond in  $Fe(CO)_5$ . The loss of a CO ligand is expected to remove only a small fraction of the excess internal energy of  $Fe(CO)_5^*$  [12]. Thus  $Fe(CO)_4^*$  is formed with excess internal energy and decomposes immediately into CO and Fe(CO)<sup>\*</sup><sub>3</sub>, because the Fe-C bond dissociation energy (D(Fe-C)) for  $Fe(CO)_4$  is only 5 kcal mol<sup>-1</sup> [13]. Fe(CO)<sup>\*</sup><sub>3</sub> decomposes in a similar manner, either sequentially or via absorption of laser light. The coordinatively highly unsaturated species,  $Fe(CO)_m$  ( $m \leq 3$ ), still possess CO ligands and, therefore, may absorb IR laser light at 16  $\mu$ m.

Fe (CO)<sub>m</sub> may be produced with a large internal energy and be in a quasi-continuum region. Thus Fe (CO)<sub>m</sub> will absorb laser light efficiently even if the fundamental absorption bands of Fe (CO)<sub>m</sub> are not in good coincidence with the laser line. It has been recently reported that D(Fe-C) for the series of Fe (CO)<sub>5</sub>, Fe (CO)<sub>4</sub>, Fe (CO)<sub>3</sub>, Fe (CO)<sub>2</sub>, and Fe (CO) are 55, 5, 32, 23, and 23 kcal mol<sup>-1</sup>, respectively [13]. D(Fe-C)of the coordinatively unsaturated species is considerably less than that for Fe(CO)<sub>5</sub>. This order of D(Fe-C) suggests that the secondary IRMPD produces the coordinatively unsaturated species very efficiently resulting in bare metallic iron and CO as final products.

It is concluded that a parallel laser beam at 16  $\mu$ m at low fluence can initiate fast decarbonylation of Fe(CO)<sub>5</sub> and yield CO and iron metal as products. The catalytic properties of the reaction intermediates produced in IRMPD of Fe(CO)<sub>5</sub> are now under extensive investigations.

#### References

- G.L. Geoffroy and M.S. Wrighton, Organometallac photochemistry (Academic Press, New York, 1979).
- [2] J.T. Yardley, G. Gitlin, G. Nathanson and A.M. Rosan, J. Chem. Phys. 74 (1981) 370, and references therein.
- [3] G.P. Smith and R.M. Laine, J. Phys. Chem. 85 (1981) 1620.
- [4] N.J. Bristow, B.D. Moore, M. Poliakoff, G.J. Ryott and J.J. Turner, J. Organomet, Chem. 260 (1984) 181.
- [5] P.A. Teng, F.D. Lewis and E. Weitz, J. Phys. Chem. 88 (1984) 4895.
- [6] Y. Langsam and A.M. Ronn, Chem. Phys. 54 (1981) 277.
- [7] M.-K. Au, P.A. Hackett, M. Humphries and P. John, Appl. Phys. B33 (1984) 43.
- [8] L.H. Jones, R.S. McDowell, M. Goldblatt and B.I. Swanson, J. Chem. Phys. 57 (1972) 2050.
- [9] K. Midorikawa, H. Tashiro, Y. Aoki, K. Phashi, K. Nagasaka, K. Toyoda and S. Namba, J. Appl. Phys. 57 (1984) 1504.
- [10] P. Rabinowitz, A. Stein, R. Brickman and A. Kaldor, Appl. Phys. Letters 35 (1979) 739.
- [11] W.P. Griffith, in: Comprehensive inorganic chemistry, Vol. 4 (Pergamon Press, Oxford, 1973) p. 1205.
- [12] J.T. Yardley, G. Gitlin, G. Nathanson and A.M. Rosan, J. Chem. Phys. 74 (1981) 370.
- [13] P.C. Engelking and W.C. Lineberger, J. Am. Chem. Soc. 101 (1979) 5569.