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Title

Unusually Slow Photo-dissociation of CO from (η^6 -C₆H₆)Cr(CO)₃ (M = Cr or Mo); a Time Resolved Infrared, Matrix Isolation and DFT Investigation

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B3LYP/LANL2DZ

Comparison of calculates geometric parameters for (eta-6-Benzene)Cr(CO)3 with experimental values from literature

Bond Lengths (A)

	Calculated	Literature(a)
Cr-C(Arene)	2.3087	2.223
C-H	1.0843	1.113
Cr-C(O)	1.8317	1.845
C-O	1.188	1.157

Bond Angles (o)

	Calculated	Literature(a)
C-C-C	119.3236	120.07
C-Cr-C(Arene)	75.9189	

(a) Hunter, A.D.; Shilliday, L. Organometallics, 1992, 11, 1550.

B3LYP/LANL2DZ

TDDFT excited state calculations on (eta-6-Benzene)Cr(CO)3

State	E eV(nm)	Osc.Strength	K-S Orbitals	%
1	3.1974(387.76)	0.0000	48 - 50 48 - 53 48 - 62 49 - 51	22 24 22 24
2	3.2826(377.70)	0.0014	47 - 52 48 - 51 49 - 50	29 29 29
3	3.2827(377.69)	0.0014	47 - 53 48 - 50 49 - 51	29 29 28
4	3.3230(373.11)	0.0000	48 - 50 48 - 53 49 - 51 49 - 52	25 21 26 21
5	3.3431(370.87)	0.0000	48 - 52 49 - 53	48 42
6	3.4569(358.66)	0.0016	47 - 51 47 - 52 48 - 51 49 - 50	12 25 20 20
7	3.4570(358.64)	0.0016	47 - 50 47 - 53 48 - 50 49 - 51	12 25 20 19
8	3.5966(344.73)	0.0013	47 - 51	74
9	3.5967(344.71)	0.0013	47 - 50	73

10	3.7449(331.07)	0.0001	47 - 52 48 - 52 49 - 53	25 25 25
11	3.7449(331.07)	0.0001	47 - 53 48 - 53 49 - 52	25 25 25
12	3.9892(310.80)	0.0015	48 - 54	86
13	3.9892(310.79)	0.0015	49 - 54	86
14	4.1654(297.65)	0.1893	48 - 51 49 - 50	36 36

Contributions of Cr, CO, and Benzene to selected K-S Orbitals in (eta-6-Benzene)Cr(CO)₃

Orbital	Cr%	CO%	Benzene%
63	94	4	2
62	50	43	7
61	50	43	7
60	89	8	3
59	0	100	0
58	74	20	7
57	74	20	7
56	28	70	2
55	28	70	2
54	45	53	2
53	51	42	7
52	51	42	7
51	4	11	85
50	4	11	85
49	61	27	12
48	61	27	12
47	73	26	2
46	11	4	85
45	11	4	85
44	12	72	16
43	12	72	16
42	4	44	52

Quantum Yield Determinations

Molar Absorption Coefficients for (Benzene)Cr(CO)₃

Epsilon₃₅₅ = 3,060

Epsilon₃₁₆ = 11,500

Irradiation at 365.6 nm

Reduction in intensity of band at 316 nm = 0.32 for 2 minute irradiation (cyclooctene trapping ligand)

Molar reduction = 2.78×10^{-5} molar

For a 3 cm³ sample the number of moles photolysed = 8.34×10^{-8} moles

Number of molecules photolysed = 5.02×10^{16}

Absorbance at 365 = 0.37 implying 57% of light absorbed by sample at this wavelength

Change in absorbance of actinometer solution at 510 nm = 0.193

Number of Fe²⁺ ions = 1.57×10^{17} ions

Using a quantum yield for Fe²⁺ production of 1.26 at 365.6 nm

Number of photons emitted by the source at 365.6 nm is 1.24×10^{17}

Light intensity = 1×10^{-7} ein/min

Number of photons absorbed by the sample in 2 minutes is 7.07×10^{16}

Quantum yield of photochemical reaction = 0.71

Molar Absorption Coefficients for (Benzene)Cr(CO)₃

Epsilon₃₅₅ = 3,060

Epsilon₃₁₆ = 11,500

Irradiation at 254 nm

Reduction in intensity of band at 316 nm = 0.46 for 90 minute irradiation (cyclooctene trapping ligand)

Molar reduction = 4.0×10^{-5} molar

For a 3 cm³ sample the number of moles photolysed = 1.2×10^{-7} moles

Number of molecules photolysed = 7.5×10^{16}

Absorbance at 254 = 0.7 implying 80% of light absorbed by sample at this wavelength

Change in absorbance of actinometer solution at 510 nm = 0.26

Number of Fe²⁺ ions produced = 2.12×10^{17} ions

Using a quantum yield for Fe²⁺ production of 1.25 at 365.6 nm

Number of photons emitted by the source at 254 nm is 1.69×10^{17}

Light intensity 3.12×10^{-9} ein/min

Number of photons absorbed by the sample in 90 minutes is 1.35×10^{17}

Quantum yield of CO-loss reaction = 0.56