Kinetic Study of the Interconversion of the Regio-isomeric Iron Tricarbonyl Complexes Derived from 4-Bromotropone

Martin G. Banwell* and Hans M. Schuhbauer

Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, ACT 0200, Australia

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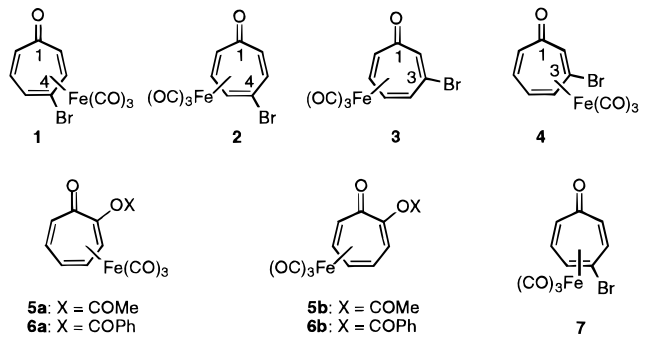
Summary: The title complexes, ***1*** *and* ***2****, have been prepared and their interconversion has been studied by* ^{1}*H NMR spectroscopy; the activation enthalpies and entropies as well as the equilibrium constants for these reversible intramolecular first-order processes have been determined. The iron tricarbonyl complex* ***3*** *of 3-bromotropone has also been prepared, but this does not isomerize to regio-isomer* ***4****.*

Tropone (2,4,6-cycloheptatrien-1-one) normally undergoes 1,8-addition reactions with nucleophiles[1] and engages, as the 6π-addend, in [π6s + π4s] cycloadditions with conjugated dienes.[2] In contrast, the η^4-iron tricarbonyl complex of this seven-membered carbocycle reacts in a 1,2- or 1,4-fashion with nucleophiles[3] and participates, as the 2π-addend, in a range of [π4s + π2s] (Diels−Alder) cycloaddition reactions.[3] Furthermore, the presence of the coordinating iron tricarbonyl unit imposes high levels of diastereofacial selection on these latter processes.[3−5] As a consequence of such features (2−5-η)-(tropone)iron tricarbonyl is being exploited, on an increasing basis, in chemical synthesis. This trend is highlighted in recent preparations of derivatives of the biologically active heptitols[4] and calystegines.[5]

While the parent complex has been known since 1959,[6] only a handful of examples of 2- and 4-substituted (tropone)iron tricarbonyl compounds have been described in the literature.[7] Furthermore, there appears to be no report of any 3-substituted derivative. The reduction in the symmetry of the tropone ring due to monosubstitution (at any of the positions C-2, C-3, or C-4) creates the potential for formation of two regio-isomeric complexes. Indeed, Rosenblum and Watkins[7f] have noted the occurrence of two separable (4-methyltropone)iron tricarbonyl complexes, while Morita and Asao[7b−d,g] have isolated various regio-isomeric 2-substituted systems. Like a number of related species,[8] such troponoid derivatives often exhibit fluxional behavior and the energetics associated with the interconversion of various regio-isomeric pairs of substituted tropone iron tricarbonyl complexes have been determined.[7] In anticipation of certain synthetic studies, we required the previously unreported iron tricarbonyl complexes derived from 3- and 4-bromotropone. For our purposes it was crucial to establish what preference, if any, might be shown for formation of one regio-isomer over the other and, if such systems did exhibit fluxional behavior, what the energetics of interconversion of these isomers might be. The results of such a study are reported herein.

Chart 1



Syntheses of the desired iron tricarbonyl complexes were achieved in a straightforward manner. Thus, reaction of 4-bromotropone[9] with diiron nonacarbonyl in refluxing benzene yielded the expected pair of regio-isomeric complexes **1** (29% yield) and **2** (35% yield) (see Chart 1) which could be readily separated from one another by flash chromatography on silica. Reaction of 3-bromotropone[9] under similar conditions led to compound **3** (5.7% yield) as the only isolable product. Since the outer carbons and any attached protons of (diene)-$Fe(CO)_3$ complexes are significantly shielded relative to their uncomplexed counterparts,[10] the structures of compounds **1**−**3** were readily assigned by ^{1}H and ^{13}C NMR spectroscopic methods (Tables 1 and 2). For example, in the ^{1}H NMR spectrum of the chromato-

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Table 1. 300 MHz ^{1}H NMR Data (ppm, Hz) for Complexes 1−3 (in Acetone-d_6)

complex	H-2	H-3/H-4	H-5	H-6	H-7
1	3.11 (dd); $J_{2,3} = 7.8$, $J_{2,7} = 2.1$	7.01 (dd); $J_{3,5} = 1.8$	3.46 (ddd); $J_{5,6} = 8.2$, $J_{5,7} = 0.9$	6.73 (dd); $J_{6,7} = 10.9$	5.03 (ddd)
2	4.97 (dd); $J_{2,3} = 11.6$, $J_{2,7} = 2.4$	7.06 (d)	7.20 (dd); $J_{5,6} = 5.2$, $J_{5,7} = 1.2$	6.67 (dd); $J_{6,7} = 7.8$	3.23 (ddd)
3	5.52−5.62 (m)	3.18−3.27 (b, d); $J_{4,5} = 6.4$	6.24−6.36 (m)	6.24−6.36 (m)	3.06−3.13 (b, d); $J_{6,7} = 7.9$

Table 2. 75 MHz ^{13}C NMR Data (ppm) for Complexes 1−3 (in $CDCl_3$)

complex	C-1	C-2	C-3	C-4	C-5	C-6	C-7	$(OC)_3$Fe
1	197.9	55.3[a]	94.4	103.2	54.7[a]	146.5	122.9	203.4, 202.8
2	197.0	120.6	152.6	59.4	100.4	88.5	62.4	203.5
3	194.9	124.6	146.5	60.5	93.2[b]	92.4[b]	56.9	

[a,b] Values with the same superscript may be interchanged.

Table 3. Kinetic Data for the Interconversion of Complexes 1 and 2 in Acetone-d_6 at Different Temperatures ($K_{eq} = k_{-1}/k_1$)

temp, K	[**1**]^0, 10^{-2} mol L^{-1}	[**2**]^0, 10^{-2} mol L^{-1}	K_{eq}	k_1, 10^{-7} s^{-1}	k_{-1}, 10^{-7} s^{-1}
323.15	1.55	0	0.995	56.7	56.4
	0	3.09	0.994	56.7	56.4
313.15	4.45	0	0.945	19.6	18.6
	0	2.26	0.946	19.6	18.5
303.15	4.00	0	0.856	5.07	4.34
	0	3.92	0.857	5.07	4.35

graphically more mobile complex derived from 4-bromotropone two high-field resonances are observed at δ 3.11 (dd, $J = 7.8$ and 2.1 Hz) and 3.46 (ddd, $J = 8.2$, 1.8 and 0.9 Hz). These data can only be accommodated by structure **1**, and the resonances just mentioned are assigned to H-2 and H-5, respectively. By contrast, in the ^{1}H NMR spectrum of the less mobile complex there is only one high-field resonance, a doublet of doublet of doublets ($J = 7.8$, 2.4 and 1.2 Hz) at δ 3.23, and this must be assigned to H-7 in structure **2**. In the ^{1}H NMR spectrum of the single complex isolated from the reaction of 3-bromotropone with diiron nonacarbonyl two high-field doublets are observed at δ 3.10 and 3.22 ($J = 7.9$ and 6.4 Hz, respectively). This suggests that both of the outer protons associated with the (diene)iron tricarbonyl subunit are vicinally related to other protons, a situation which can be accommodated by structure **3** but not **4**.

All three complexes were stable in the crystalline state, but in solution at ambient temperatures compounds **1** and **2** slowly interconverted. This isomerization process was monitored by ^{1}H NMR spectroscopy in acetone-d_6 at different temperatures, and the rate constants for the forward (**1** → **2**) and backward (**2** → **1**) reactions, k_1 and k_{-1}, respectively, were determined (Table 3). Using the theory of the activated complex,[11] the thermodynamic parameters for this interconversion could be calculated from the tabulated data. Values for **1** → **2** (**2** → **1**) at 323.15 K are $\Delta G^{\ddagger} = 26.7$ kcal mol^{-1} (26.7 kcal mol^{-1}), $\Delta H^{\ddagger} = 22.9$ kcal mol^{-1} (24.3 kcal mol^{-1}), and $\Delta S^{\ddagger} = -11.8$ cal K^{-1} mol^{-1} (−7.3 cal K^{-1} mol^{-1}).

These data are usefully compared with literature values for related processes. Thus, in their study of the racemization of chiral (tropone) iron tricarbonyl in isooctane at 338.15 K Tajiri *et al.*[12] determined that $\Delta G^{\ddagger} = 25.5$ kcal mol^{-1}, $\Delta H^{\ddagger} = 25.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -1.2$ cal K^{-1} mol^{-1}, and $k_1 = 2.7 \times 10^{-4}$ s^{-1}. Morita and coworkers[7c] have presented equivalent data for the interconversion, in $CDCl_3$ at 323.15 K, of (2-acetoxytropone)iron tricarbonyls **5a**,**b** as well as (2-benzoyloxytropone)iron tricarbonyls **6a,b**; values for **5b** → **5a** (**6b** → **6a**) are $\Delta G^{\ddagger} = 25.3$ kcal mol^{-1} (25.4 kcal mol^{-1}), $\Delta H^{\ddagger} = 26.1$ kcal mol^{-1} (30.1 kcal mol^{-1}), $\Delta S^{\ddagger} = +2.4$ cal K^{-1} mol^{-1} (+14.6 cal K^{-1} mol^{-1}), $k_{-1} = 2.4 \times 10^{-5}$ s^{-1} (2.4×10^{-5} s^{-1}), and $K_{eq} = 0.67$ (0.67). Interestingly, 2-((trimethylsilyl)oxy)tropone[7c] is reported to form only the (4−7-η)-complex equivalent to **5b** or **6b**, and this does not isomerize to the alternate regio-isomer under normal conditions. Such comparisons imply that introduction of a bromo substituent at C-4 on the troponoid ring results in a relatively high activation barrier for the interconversion of the regio-isomeric iron tricarbonyl complexes **1** and **2**. The negative activation entropies for both the forward and backward reactions clearly contribute, in a major way, to the high value of $\Delta G^{\ddagger}$. A likely explanation is that developing steric interactions between the iron and bromine atoms play a significant role as the iron tricarbonyl fragment moves toward the central (4,5-) double bond during the isomerization process. It should be noted that negative activation entropies have been determined for related isomerizations involving nondissociative mechanisms. Thus, in addition to the case mentioned above (*viz.* the racemization of enantiopure (tropone)iron tricarbonyl[12]) Knoelker *et al.*[13] have very recently examined the rate of epimerization of a (η^4-1-aza-1,3-butadiene)iron tricarbonyl derivative and from the kinetic data presented the activation parameters turn out to be $\Delta H^{\ddagger} = 21.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.2$ cal K^{-1} mol^{-1}. These authors propose an intramolecular mechanism, involving a η^1-imine species, for this epimerization process.

The polarity and/or ligand donor abilities of the reaction medium appear to have little effect on the rate of interconversion of complexes **1** and **2**. Thus, this isomerization process was monitored in a range of different solvents and the values of k_1 and k_{-1} were shown (Table 4) to change by less than a factor of 2.5. In all cases, the rate and equilibrium constants for the interconversions were clearly independent of the initial concentrations. It must be concluded, therefore, that these reactions (*viz.* **1** → **2** and **2** → **1**) are reversible intramolecular first-order processes in which the surrounding medium has only a minor impact on rate. By analogy with other proposals,[8,12] we suggest that the 16-electron η^2-iron species **7** lies on the reaction pathway associated with the interconversion of **1** and **2**.

Our failure to generate complex **4** in the reaction of 3-bromotropone with diiron nonacarbonyl made at-

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Table 4. Kinetic Data for the Interconversion of Complexes 1 and 2 in Different Solvents at 323.15 K ($K_{eq} = k_{-1}/k_1$)

solvent	$[\mathbf{1}]^0$, 10^{-2} mol L^{-1}	$[\mathbf{2}]^0$, 10^{-2} mol L^{-1}	K_{eq}	k_1, 10^{-7} s^{-1} (k_{rel})[a]	k_{-1}, 10^{-7} s^{-1} (k_{rel})[a]
acetic-d_4 acid	2.30	0	0.688	134.8 (2.38)	92.8 (1.65)
	0	3.84	0.688	134.7 (2.38)	92.6 (1.64)
benzene-d_6	2.74	0	1.018	103.7 (1.83)	105.5 (1.87)
	0	2.35	1.015	103.9 (1.83)	105.5 (1.87)
$CDCl_3$	3.42	0	1.354	72.8 (1.28)	98.6 (1.75)
	0	2.45	1.356	72.8 (1.28)	98.6 (1.75)
acetone-d_6	1.55	0	0.995	56.7 (1.00)	56.4 (1.00)
	0	3.09	0.994	56.7 (1.00)	56.4 (1.00)

[a] Relative to the values obtained in acetone-d_6.

tempts to produce this material by isomerization of regio-isomer **3** all the more crucial. However, compound **3** only showed slow decomposition in acetone-d_6 at 313.15 K for 50 d. The reasons for this situation remain unclear at the present time.

Experimental Section

All reactions were performed using distilled solvents. Acetic-d_4 acid, acetone-d_6, benzene-d_6, and $CDCl_3$ were deoxygenated with nitrogen prior to use. $Fe_2(CO)_9$ (Aldrich) was stored at −30 °C before use. 3- and 4-Bromotropone were prepared from cyclohexa-1,4-diene (Aldrich) according to established procedures.[9] Infrared and electronic spectra were run on Perkin-Elmer 683 and Hewlett-Packard 8450A instruments, respectively. Electron-impact mass spectra were performed on a Fisons Instruments VG AutoSpec (magnet scans for low-resolution spectra and voltage scans for high-resolution spectra), and elemental analyses were carried out on a Carlo-Erba 1106 elemental analyzer. ^{13}C- and ^1H-NMR spectra were recorded on Varian Gemini-300 or VRX300S spectrometers, the latter with variable-temperature control (±1 °C) and calibration using the temperature dependence of the ^1H NMR signals of ethylene glycol and methanol. Chemical shifts are reported in parts per million (ppm) and were determined by reference to the appropriate solvent signal, *viz.*, δ 2.03 for acetic-d_4 acid, δ 2.17 for acetone-d_6, δ 7.15 for benzene-d_6 or δ 7.24 for $CDCl_3$ in ^1H NMR experiments and δ 77.0 for $CDCl_3$ in ^{13}C NMR experiments.

(a) Synthesis of (2−5-η-4-Bromotropone)iron Tricarbonyl (1) and (4−7-η-4-Bromotropone)iron Tricarbonyl (2). 4-Bromotropone (395 mg, 2.13 mmol) and $Fe_2(CO)_9$ (2.01 g, 5.53 mmol) were dissolved in benzene (20 mL), and the resulting solution was heated at reflux under a nitrogen atmosphere for 2 h. After cooling, the reaction mixture was filtered (No. 3 sintered glass funnel) and the solid thus retained washed thoroughly with benzene. The combined and bright red filtrate was concentrated under reduced pressure, and the resulting red oil was subjected to flash chromatography (silica gel, 1:4 ethyl acetate/hexane elution). In this manner three fractions, A−C, were obtained.

Concentration of fraction A (R_f = 0.25) afforded 4-bromotropone (65 mg, 16% recovery) which was identical, in all respects, with authentic material.

Concentration of fraction B (R_f = 0.5) afforded complex **2** (200 mg, 35% at 84% conversion) as a bright orange solid, mp 76−79 °C: ν_{max} (KBr) 3040, 2070, 2000, 1623, 1595, 1450, 1390, 1360, 1272, 1172, 1150, 920, 845, 795, 725, 699, 610, and 592 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; mass spectrum (EI, 30 eV) *m*/*z* 296/298 ($M^{+\bullet}$ − CO, 18%), 268/270 ($M^{+\bullet}$ − 2CO, 51), 240/242 ($M^{+\bullet}$ − 3CO, 39), 212/214 ($M^{+\bullet}$ − 4CO, 13), 184/186 [$M^{+\bullet}$ − $Fe(CO)_3$, 10], 156/158 [$M^{+\bullet}$ − $Fe(CO)_3$ − CO, 10], 132 (100), 106 (20), 77 (32); MS (CI) *m*/*z* 325/327 (MH^+, 100%), 257/259 (50), 107.1 (94); HRMS (EI) *m*/*z* calcd for $C_9H_5{}^{79}Br^{56}FeO_3$ ($M^{+\bullet}$ − CO) 295.8771, found 295.8778. Anal. Calcd for $C_{10}H_5BrFeO_4$: C, 37.0, H, 1.6, Br, 24.6. Found: C, 37.4, H, 1.3, Br, 24.6.

Concentration of fraction C (R_f = 0.7) afforded complex **1** (170 mg, 29% at 84% conversion) as a bright orange solid, mp 85.5−87 °C: ν_{max} 3035, 2075, 2025, 2010, 1990, 1960, 1630, 1610, 1450, 1402, 1385, 1365, 1312, 1275, 1190, 1140, 1075, 935, 860, 850, 785, 710, 618, 590, 555 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; MS (EI, 30 eV) *m*/*z* 324/326 ($M^{+\bullet}$, 1%), 296/298 ($M^{+\bullet}$ − CO, 17), 268/270 ($M^{+\bullet}$ − 2CO, 47), 240/242 ($M^{+\bullet}$ − 3CO, 40), 212/214 ($M^{+\bullet}$ − 4CO, 11), 184/186 [$M^{+\bullet}$ − $Fe(CO)_3$, 10], 156/158 [$M^{+\bullet}$ − $Fe(CO)_3$ − CO, 12], 132 (100), 106 (25), 77 (55); HRMS (EI) *m*/*z* calcd for $C_{10}H_5{}^{79}Br^{56}FeO_4$ ($M^{+\bullet}$) 323.8721, found 323.8727; calcd for $C_{10}H_5{}^{81}Br^{56}FeO_4$ ($M^{+\bullet}$) 325.8700, found 325.8713. Anal. Calcd for $C_{10}H_5BrFeO_4$: C, 37.0, H, 1.6, Br, 24.6. Found: C, 36.9, H, 1.2, Br, 24.4.

(b) Synthesis of (4−7-η-3-Bromotropone)iron Tricarbonyl (3). Reaction of 3-bromotropone (550 mg, 2.97 mmol) and $Fe_2(CO)_9$ (2.76 g, 7.59 mmol) in refluxing benzene (35 mL) in the manner described above provided a red oil on workup. Subjection of this material to flash chromatography (silica gel, 1:4 ethyl acetate/hexane elution) then afforded, after concentration of the appropriate fraction (R_f = 0.4), complex **3** (55 mg, 5.7%) as orange crystals, mp 67−72 °C: ν_{max} 3050, 2070, 1995, 1620, 1410, 1380, 1310, 1272, 1162, 1130, 920, 890, 880, 835, 760, 705, 612, 598, 560 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; MS (EI, 30 eV) *m*/*z* 324/326 ($M^{+\bullet}$, 3%), 296/298 ($M^{+\bullet}$ − CO, 32), 268/270 ($M^{+\bullet}$ − 2CO, 65), 240/242 ($M^{+\bullet}$ − 3CO, 40), 212/214 ($M^{+\bullet}$ − 4CO, 25), 156/158 [$M^{+\bullet}$ − $Fe(CO)_3$ − CO, 13], 132 (100), 106 (20), 77 (40); HRMS (EI) *m*/*z* calcd for $C_9H_5{}^{79}Br^{56}FeO_3$ ($M^{+\bullet}$ − CO) 295.8771, found 295.8775; calcd for $C_9H_5{}^{81}Br^{56}FeO_3$ ($M^{+\bullet}$ − CO) 297.8751, found 297.8752. Satisfactory microanalytical data could not be obtained for this compound.

(c) Kinetic Measurements Associated with the Interconversion of Complexes 1 and 2. Pure (>99% ^1H NMR analysis) complex **1** or **2** was dissolved in degassed solvent (1.00 mL), and the isomerization was monitored, at the temperatures specified in Tables 3 and 4, by ^1H NMR techniques. The times required for solution preparation and signal accumulation were deemed to be insignificant. In all but one instance, reactions were followed to equilibrium by integration of the signals due to H-7 in **1** and H-2 in **2** [exception: the interconversion in benzene-d_6 was monitored by integrating the signals at δ 2.38 (H-2 in **1**) and δ 4.65 (H-2 in **2**)]. After conversion into concentrations, 24−63 values for k_{obs} ($=k_1 + k_{-1}$) were obtained from a plot of $\ln[(A^0 - A^\infty)/(A^t - A^\infty)]$ *vs* time (parameter *A* represents the concentration of complex **1**), using a linear least-squares computer simulation. Determination of A^∞ provided the equilibrium constants: $K_{eq} = A^\infty/(A^0 - A^\infty)$.

Compounds **1**−**3** readily dissolved in common organic solvents and underwent slow decomposition in solution. Since regio-isomers **1** and **2** interconvert *via* a first-order kinetic process (see main section), the partial decomposition of these complexes did not affect the kinetic studies detailed here.

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