The Migration of the Cr(CO)$_3$ Unit from the Eight- to the Six-membered Ring in Benzocyclo-octatetraene

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Rate constants and activation parameters have been measured for the migration of Cr(CO)$_3$ from the eight- to the six-membered ring of benzocyclo-octatetraene in decalin and n-butyl ether.

In recent years a number of experimental studies[1] and a major theoretical one[2] have been dedicated to the haptotropic rearrangement of an ML_n group in bicyclic polyenes. The reported examples deal mainly with charged species [fluorenyl, indenyl, and benzocycloheptatrienyl anions complexed with Cr(CO)$_3$]. To our knowledge kinetic data on this interesting fluxional process in neutral hydrocarbons are available only for one very recent case, the naphthalene-Cr(CO)$_3$ system.[3] The publication of the kinetic data on this rearrangement prompted us to report our kinetic data on the metal migration in another neutral system, the benzocyclo-octatetraene-Cr(CO)$_3$. The occurrence of this rearrangement was predicted in the theoretical paper by Albright *et al.*[2]

The migration of the Cr(CO)$_3$ unit from the eight- to the six-membered ring in benzocyclo-octatetraene (Scheme 1) was studied in decalin and n-butyl ether at temperatures between 428 and 454 K.

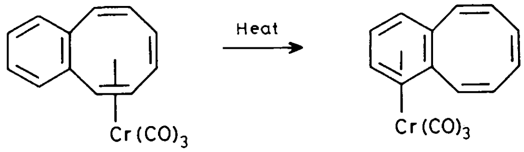
Complex (**1**) was prepared by reacting benzocyclo-octatetraene with (NH$_3$)$_3$Cr(CO)$_3$ in tetrahydrofuran (THF) at reflux for 5 h, while more drastic conditions were required for the preparation of (**2**): Cr(CO)$_6$ in n-butyl ether–THF 90 : 10 at 120 °C for 24 h.[†]

In solution, the yellow complex, (**2**), is thermally stable while the red complex, (**1**), undergoes isomerization to (**2**) along with some decomplexation. Isomerization is favoured at higher temperatures (T 150 °C) when n-butyl ether is used as solvent. [The rate of decomplexation of (**2**) is much lower than that of complex (**1**).] The kinetics are measured by monitoring the decrease of the reagent (**1**) as well as the increase of the product (**2**) by h.p.l.c. analysis and good overall first-order rate constants, $k_{obs.}$, are obtained. The kinetic data and the activation parameters are given in Table 1 where the rate constants for isomerization, $k_{isom.}$, and for decomplexation, $k_{decompl.}$, have been calculated by taking into account the yield of isomerization.

The order of the reaction together with the low values of the entropy of activation in both solvents are consistent with an intramolecular mechanism for the rearrangement. Further support in favour of an intramolecular mechanism comes from competitive experiments carried out in the presence of ligands with extraordinary complexation ability;[4] thus, when the isomerization (**1**)→(**2**) was carried out in the presence of a large excess of hexamethylbenzene, no cross products could be identified. Moreover, the low value of the solvent effect [$k_{isom.}$ (n-butyl ether)/$k_{isom.}$ (decalin) = 2.3] is in accord with the formation of a non-polar transition state.

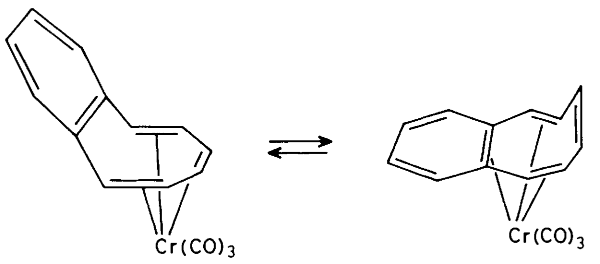
The activation energies in the two solvents (Table 1) are very close to the values obtained for the haptotropic migration of the Cr(CO)$_3$ in dimethoxy and dimethyl naphthalene complexes[3] ($\Delta H^{\ddagger}$ = 28 and 30 kcal/mol, respectively). In the theoretical investigation[2] an electron counting method was proposed to determine which of the possible reaction pathways for the migration of the ML_n unit in a bicyclic system is allowed and which is forbidden. According to this method, in the naphthalene complex ($4q+2$ π-electrons) the least-motion path across the carbon–carbon fusion bond is forbidden, whereas in the benzocyclo-octatetraene complex ($4q$ π-electrons) it should be partially allowed. At first glance, the similarities between the activation parameters for the haptotropic shift in two systems differing both in number of electrons and geometry may seem surprising. However, it is possible to hypothesize a process in which there is a pre-equilibrium between structures (A) and (B) (Scheme 2). Structure (B) is electronically similar to the naphthalene complex, which would explain the similarity of the activation parameters. Alternatively, the least-motion path through the carbon–carbon bond should be the operative one.

In contrast to the naphthalene complexes, where concurrent decomposition is not observed,[3] in our system decomposition competes favourably with isomerization. It is worth noting that whereas in decalin the two reactions show almost identical activation parameters, in n-butyl ether there is a difference both in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. This is consistent with solvation being more important for decomposition than for isomerization when n-butyl ether is the solvent.



(**1**) (**2**)

Scheme 1



(A) (B)

Scheme 2

[†] Compound (**1**), red crystals, m.p. 130 °C (decomp.); compound (**2**), yellow crystals, m.p. 92—93 °C. Satisfactory C and H microanalyses were obtained for both compounds. Selected spectroscopic data: (**1**), i.r.: ν(CO) (KBr) 1973s, 1923s, 1901s cm^{-1}; u.v. (cyclohexane) λ_{max} (ε): 250 (9200), 335 (10800), and 410 nm (2100); ^{1}H n.m.r. ([^{2}H$_6$]acetone; δ): 6.7—7.0 (4H, aromatic AA′BB′ m), 6.5 (2H, olefinic), 5.2—5.6 (4H, olefinic); mass spectrum m/z 290 (M^+).

Compound (**2**) i.r.: ν(CO) (KBr) 1965s, 1889s cm^{-1}; u.v. (cyclohexane) λ_{max} (ε): 240sh (22200), 280sh (8700), 305 (7130) and 340 nm (6700); ^{1}H n.m.r. ([^{2}H$_6$]acetone; δ): 5.4—5.7 (4H aromatic, AA′BB′ m), 6.0—6.4 (6H, olefinic); mass spectrum m/z 290 (M^+).

The structures of (**1**) and (**2**) were determined by X-ray analysis and will be published elsewhere along with detailed n.m.r. data.

Table 1. Rate constants and activation parameters.

Solvent: decalin[a]

T(K)	$10^3k_{\mathrm{obs.}}$ (s^{-1})	$10^3k_{\mathrm{isom.}}$ (s^{-1})	$10^3k_{\mathrm{decompl.}}$ (s^{-1})	% Isomerization
428 ± 0.5	1.09 ± 0.07	0.88 ± 0.06	0.21 ± 0.01	81.1
438 ,,	2.70 ± 0.22	2.20 ± 0.18	0.50 ± 0.04	81.5
448 ,,	4.59 ± 0.08	3.72 ± 0.06	0.87 ± 0.02	81.0
453 ,,	8.26 ± 0.24	6.66 ± 0.20	1.59 ± 0.05	80.6
at 443 K:	$\Delta H^\ddagger$ (isom.) = 28.8 ± 1.8 kcal/mol,[b]		$\Delta S^\ddagger$ (isom.) = −6.0 ± 4.0 e.u.[c]	
	$\Delta H^\ddagger$ (decompl.) = 28.8 ± 1.7 kcal/mol,[b]		$\Delta S^\ddagger$ (decompl.) = −8.8 ± 3.9 e.u.[c]	

Solvent: n-butyl ether[a]

T(K)	$10^3k_{\mathrm{obs.}}$ (s^{-1})	$10^3k_{\mathrm{isom.}}$ (s^{-1})	$10^3k_{\mathrm{decompl.}}$ (s^{-1})	% Isomerization
433 ± 0.5	4.14 ± 0.09	2.95 ± 0.06	1.19 ± 0.03	71.3
443 ,,	8.85 ± 0.52	6.65 ± 0.39	2.20 ± 0.13	75.2
454 ,,	21.7 ± 0.65	16.7 ± 0.50	5.03 ± 0.15	76.8
at 443 K:	$\Delta H^\ddagger$ (isom.) = 31.4 ± 1.0 kcal/mol,[b]		$\Delta S^\ddagger$(isom.) = 1.6 ± 2.2 e.u.[c]	
	$\Delta H^\ddagger$ (decompl.) = 26.0 ± 1.4 kcal/mol,[b]		$\Delta S^\ddagger$(decompl.) = −12.8 ± 3.1 e.u.[c]	

[a] The concentration of the reagent (**1**) is 4 × 10^{-3} M in all experiments; the vials are sealed under argon., [b] 1 kcal = 4.184 kJ. [c] e.u. entropy unit = cal mol^{-1} K^{-1}.

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References

1 K. M. Nicholas, R. C. Kerber, and E. I. Steifel, *Inorg. Chem.*, 1971, **10**, 1519; T. Thoma, V. G. Pleshakov, N. S. Prostakov, Yu. A. Ustynyuk, A. N. Nesmeyanov, and N. A. Ustynyuk, *J. Organomet. Chem.*, 1980, **192**, 359; A. Ceccon, A. Gambaro, G. Agostini, and A. Venzo, *ibid.*, 1981, **217**, 79; A. Ceccon, A. Gambaro, and A. Venzo, *ibid.*, 1985, **281**, 221.

2 T. A. Albright, P. Hofmann, R. Hoffmann, C. P. Lillya, and P. A. Dobosh, *J. Am. Chem. Soc.*, 1983, **105**, 3396 and references therein.

3 R. U. Kirss and P. M. Treichel, Jr., *J. Am. Chem. Soc.*, 1986, **108**, 853.

4 C. L. Zimmermann, S. L. Shaner, S. A. Roth, and B. R. Willeford, *J. Chem. Res.* (*S*), 1980, 108; (*M*), 1980, 1289.