

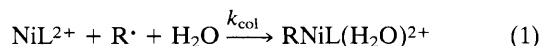
## Colligation Reactions between a Nickel(II) Macrocycle and Alkyl Radicals

Douglas G. Kelley, James H. Espenson\* and Andreja Bakac\*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011, USA

The bimolecular reaction between  $RRSS-NiL^{2+}$  (where L = 1,4,8,11-tetraazacyclotetradecane) and alkyl radicals (R $\cdot$ ) forms the organometallic species  $RNiL(H_2O)^{2+}$ , with rate constants that vary in the order Me  $\gg$  primary  $\gg$  secondary in aqueous perchloric acid at 25 °C, reflecting the decreasing strength of the nickel-carbon bond.

Colligation<sup>1</sup> reactions occur between metal complexes and alkyl radicals according to eqn. (1);  $NiL^{2+}$  is the so called *trans*-III isomer.<sup>2</sup>



The first observation<sup>3</sup> of these reactions was for the case of R $\cdot$  = Me $\cdot$ . Using organocobalt complexes<sup>4</sup> for the photochemical generation of R $\cdot$  and a kinetic probe method<sup>†</sup> with ABTS $\cdot^-$ , we were able to obtain values of  $k_{col}$  for a range of radicals, as summarized in Table 1.

The trend in values is remarkable;  $k_{col}$  varies with radical structure in the order Me  $\gg$  primary  $\gg$  secondary. However, such a trend is nearly absent for analogous reactions<sup>5,6</sup> of

chromium and cobalt complexes, also cited in Table 1. It is to be noted that the reactive  $NiL^{2+}$  complex is square planar,<sup>‡7</sup> whereas the others are five- or six-coordinate species. Thus the nickel reaction is accompanied by coordination of water, whereas those of cobalt and chromium feature a loss of a coordinated water (except for vitamin B<sub>12r</sub>, which is five-coordinate).

The thermodynamics of the metal-carbon bond formation seem to be central to determining the kinetics. The rate constants for the reverse (homolysis) reactions can be

<sup>†</sup> The persistent radical ABTS $\cdot^-$  is the one-electron oxidation product of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulphonate) ion; D. G. Kelley, J. H. Espenson and A. Bakac. *Inorg. Chem.*, 1990, **29**, 4996.

<sup>‡</sup> Actually, the species in solution are a rapidly-equilibrating mixture of four-coordinate (71%) and six-coordinate  $(H_2O)_2NiL^{2+}$  (29%).<sup>2</sup> Since the complex *cis*- $(H_2O)_2NiL^{2+}$  does not react with R $\cdot$  (A. Marchaj, unpublished observations) we conclude that the four-coordinate  $NiL^{2+}$  species, and not *trans*- $(H_2O)_2NiL^{2+}$ , is the reactant. In correcting for the abundance of the reactive form, the 'real' value of  $k_{col}$  is the value in Table 1 divided by 0.71.

**Table 1** Rate constants<sup>a</sup> ( $k_{\text{col}}/10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ ) for colligation reactions between alkyl radicals and divalent transition metal complexes in aqueous solution

R·	L <sub>n</sub> M			
	NiL <sup>2+</sup>	Cr(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup> <sup>b</sup>	(H <sub>2</sub> O) <sub>2</sub> CoL <sup>2+</sup> <sup>b</sup>	Vit. B <sub>12r</sub>
Me	73 ± 2	22	1.6	44 <sup>c,d</sup>
Et	1.3 ± 0.2	19	1.1	51 <sup>c,e</sup>
1-C <sub>3</sub> H <sub>7</sub>	1.0 ± 0.1	22	—	61 <sup>c,e</sup>
1-C <sub>4</sub> H <sub>9</sub>	1.0 ± 0.3	—	—	—
2-C <sub>3</sub> H <sub>7</sub>	<~0.02	—	—	25 <sup>f</sup>
c-C <sub>5</sub> H <sub>9</sub>	<~0.02	8	—	—

<sup>a</sup> At 25.0°C in aqueous solution with 0.10 mol dm<sup>-3</sup> HClO<sub>4</sub>. The general reaction is L<sub>n</sub>M<sup>2+</sup> + R· → RML<sub>n</sub><sup>2+</sup>, accompanying which there may be an increase in coordination number (Ni, 4–6) or not (Cr, Co). <sup>b</sup> Ref 6. <sup>c</sup> Ref 7. <sup>d</sup> pH 1.3–7. <sup>e</sup> pH 7. <sup>f</sup> pH 1.

measured for RNiL<sup>2+</sup>,<sup>3,8</sup> (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup>,<sup>5,9</sup> RCoL(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup><sup>10</sup> and organocobalamines.<sup>11</sup> From these data it is clear that the values of  $-RT \ln(k_{\text{col}}/k_{\text{hom}})$  are much smaller for NiL<sup>2+</sup> than for Co–R and Cr–R complexes. § The most favourable free energy for RNiL(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> is the case R = Me with  $K_1 \sim 10^7 \text{ l mol}^{-1}$ .<sup>3</sup> This compares with  $K_1 \sim 10^{11} \text{ l mol}^{-1}$ <sup>12</sup> for the least favourable RCrL<sup>2+</sup> analogue (R = PhCH<sub>2</sub>). The smaller the value of  $K_1$  and the lower the value of  $k_{\text{col}}$ , the larger the value of  $k_{\text{hom}}$  would be in a homologous series. This would be particularly so when at its least stable (Pr<sup>i</sup>NiL<sup>2+</sup>),  $K_1$  is no larger than *ca.* unity. These considerations hold for whatever role is played by the addition or removal of coordinate water, since this is automatically accommodated in the kinetic and thermodynamic values.

§ A complete set of data in the series Me, prim., sec. is not available for the organochromium and organocobalt complexes. The methyl derivatives usually do not homolyse ( $k_{\text{hom}}$  small), and the secondary ones are often too unstable to be prepared ( $k_{\text{hom}}$  large). This behaviour, combined with all the available kinetic data<sup>5,9–12</sup> on homolysis of the organochromium and organocobalt complexes clearly establishes the trend for  $k_{\text{hom}}$  as Me ≪ prim. ≪ sec.

The values of  $K_1$  for the organocobalt and organochromium complexes change dramatically in the series (Me > primary > secondary), without a corresponding change in the values of  $k_{\text{col}}$ , despite the fact that the values of  $k_{\text{col}}$  lie in the activation-controlled regime.<sup>12</sup> The driving force for the formation of all the alkylcobalt and alkylchromium complexes may be sufficiently large to minimise steric influences on  $k_{\text{col}}$  within each series. In support of this we note that the reverse rate constants in the uphill direction (homolysis) are dramatically influenced by steric effects for all three series.

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