Thermochimica Acta, 64 (1983) 327–336
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC INVESTIGATION OF THE COBALT(II) BROMIDE–BUTYRONITRILE AND COBALT(II) BROMIDE–ISOBUTYRONITRILE SYSTEMS

JOHN A. MAGUIRE, DON E. WELSH, JOHN J. BANEWICZ and JANET ATKINSON

Department of Chemistry, Southern Methodist University, Dallas, TX 75275 (U.S.A.)

(Received 12 November 1982)

ABSTRACT

Equilibrium decomposition pressures were measured for the $CoBr_2$–*n* C_3H_7CN and $CoBr_2$–$(CH_3)_2CHCN$ systems in the temperature range 302–348 K. For the $CoBr_2$–C_3H_7CN system, Co(*n* $C_3H_7CN)_2Br_2$ was the only stable complex formed. The values of ΔH^0 and ΔS^0 per mole of gaseous nitrile were found to be 57.7 ± 0.7 kJ mole^{-1} and 134.5 ± 2.2 J mole^{-1} K^{-1}, respectively. For the $CoBr_2$–$(CH_3)_2CHCN$ system, three stoichiometric compounds were identified. The values of ΔH^0 and ΔS^0 per mole of gaseous nitrile for the decomposition of $Co[(CH_3)_2CHCN]_nBr_2$ were found to be 64.9 ± 1.0 kJ mole^{-1} and 178.0 ± 3.3 J mole^{-1} K^{-1} for $n = 3$, 46.4 ± 0.7 kJ mole^{-1} and 114.3 ± 2.3 J mole^{-1} K^{-1} for $n = 2$, and 50.5 ± 0.7 kJ mole^{-1} and 114.3 ± 2.3 J mole^{-1} K^{-1} for $n = 1$. Standard enthalpies of formation at 298 K were calculated for these and other cobalt halide–nitrile complexes. The relative stabilities of the various complexes are discussed in terms of steric interactions.

INTRODUCTION

The solid state complexes of transition metal halides with aliphatic nitriles, especially acetonitrile, have been studied by a number of investigators [1–5]. The stabilities of the different stoichiometric phases in the CH_3CN–$CoBr_2$, CH_3CN–$CoCl_2$, and CH_3CN–$NiCl_2$ systems have been extensively studied using DTA, TG, DSC, and isoteniscopic methods [3–6]. However, the only detailed thermodynamic investigation of a higher molecular weight nitrile complex in the solid state is that reported for the C_2H_5CN–$CoBr_2$ system [5].

For all nitrile–cobalt halide systems reported so far, the stable phases with the highest nitrile content have three nitrile molecules per metal halide unit, but there is some variation in the stable phases with lower nitrile content. In the CH_3CN–$CoCl_2$ system the stoichiometric compounds are $Co(CH_3CN)_3Cl_2$, $Co(CH_3CN)_2Cl_2$ and $Co(CH_3CN)Cl_2$, while the CH_3CN–$CoBr_2$ and C_2H_5CN–$CoBr_2$ systems only form stable phases with three and two nitriles per $CoBr_2$ unit.

0040-6031/83/$03.00

The values of ΔH^0 for the removal of the nitriles are difficult to rationalize in the light of information from IR investigations of these complexes. Infrared studies indicate that in $Co(CH_3CN)_3Cl_2$ and $Co(CH_3CN)_3Br_2$ only two of the three nitriles are coordinated while in $Co(C_2H_5CN)_3Br_2$ all three nitriles are coordinated [5]. One would expect values of ΔH^0 for the removal of the uncoordinated first nitrile to be much smaller than the values of ΔH^0 for the removal of the subsequent nitriles in these complexes. Experimentally, it was found that the values of ΔH^0 for the removal of the first and second nitrile in $Co(CH_3CN)_3Cl_2$ were the same within experimental error, i.e. 47.4 ± 0.2 kJ mole^{-1} and 47.3 ± 0.3 kJ mole^{-1}, respectively. A direct comparison of the values of ΔH^0 for the removal of just the first and second nitriles is not possible in the $CH_3CN–CoBr_2$ and $C_2H_5CN–CoBr_2$ systems since neither system forms a mononitrile complex. The values of ΔH^0 per mole of nitrile for the first and second decompositions are 49.5 and 56.9 kJ mole^{-1}, respectively, for the $CH_3CN–CoBr_2$ system and 55.7 ± 0.4 and 55.0 ± 0.4 kJ mole^{-1}, respectively, for the $C_2H_5CN–CoBr_2$ system. The value of ΔH^0 for the removal of the first nitrile in $Co(CH_3CN)_3Br_2$ is somewhat smaller than the ΔH^0 per mole of nitrile for the decomposition of $Co(CH_3CN)_2Br_2$. However, the values of ΔH^0 per mole of nitrile for the decompositions of $Co(C_2H_5CN)_3Br_2$ and $Co(C_2H_5CN)_2Br_2$ are almost equal.

In the systems studied to date, there seems to be no clear correlation between the values of ΔH^0 for the removal of a nitrile and the bonding environment of the nitrile molecule. In order to obtain more information about the thermodynamic parameters of RCN–metal halide systems, an investigation of the $CH_3CH_2CH_2CN–CoBr_2$ and $(CH_3)_2CHCN–CoBr_2$ systems was undertaken. The results of this study are reported herein.

EXPERIMENTAL

Anhydrous cobalt(II) bromide was prepared from cobalt(II) carbonate and HBr as described previously [5]. The absence of peaks at 3400–3500 and 1600 cm^{-1} in the IR spectrum of this compound and subsequent complexes was taken as verification that the compounds were free of water contamination. Butyronitrile (BCN) and *iso*butyronitrile (IBN) were first dried by CaH_2 and then fractionated from a Todd column protected by phosphorus pentoxide tubes. The purified nitriles were stored over a molecular sieve (Linde 4A). The nitriles used in compound preparation showed less than 0.5 ppt water by GLC and no other impurities were detected by this method.

The procedures for the preparation and analysis of samples were the same as those used for the $CH_3CN–CoCl_2$ system [3]. Since all the compounds are quite hygroscopic, handling and transfer was done in a dry box or glove bag filled with dry nitrogen. All glassware used was pre-dried in an oven at

120°C and allowed to cool in a dry atmosphere.

Decomposition vapor pressures were determined as a function of temperature and sample composition under static conditions using isoteniscopes. Mercury was used as the manometric liquid in the IBN–$CoBr_2$ system with IBN to $CoBr_2$ molar ratios greater than one and for all compositions in the BCN–$CoBr_2$ system. The heights of mercury levels in the isoteniscopes were read to within 0.05 mm using a cathetometer and were converted to pressure using appropriate corrections [7].

For the lower stoichiometries in the IBN–$CoBr_2$ system, mercury isoteniscopic results were not reproducible and exhibited thermal hysteresis indicating that either the decomposition was not reversible or that some reaction with mercury was taking place. In view of the extremely long equilibration times for these lower complexes (1 to 2 weeks) and previous work in related systems, it was felt that the latter was the reason for the non-reproducibility and hysteresis in this system. For this reason, the decomposition vapor pressures for the IBN–$CoBr_2$ system were also measured using an isoteniscope equipped with a fused-quartz Bourdon gauge as a null indicating device in conjunction with a Ruska pressure test set (model 3876-701) for pressure regulation and measurement. This apparatus has been described in detail elsewhere [5]. In this isoteniscope the sample was suspended in the isoteniscopic chamber by a calibrated quartz spring. The isoteniscope was also fitted with a vacuum stopcock through which nitrile could be removed by pumping. This arrangement eliminated the use of mercury and allowed measurement of equilibrium vapor pressures over a wide range of compositions, all derived from a single starting sample. Equilibrium vapor pressures obtained using this apparatus were reproducible and showed no thermal hysteresis over the entire composition range studied. For samples whose IBN to $CoBr_2$ molar ratios were greater than one, decomposition vapor pressures obtained from the Bourdon gauge isoteniscope agreed with those obtained from the mercury isoteniscopes.

Equilibrium decomposition pressures as a function of temperature were measured for seven samples with IBN to $CoBr_2$ molar ratios ranging from 0.77 to 3.0 and for three samples with BCN to $CoBr_2$ molar ratios ranging from 0.28 to 1.83.

Thermogravimetric and DTA measurements were made using a DuPont Model 950 thermogravimetric analyzer and a DuPont Model 900 differential thermal analyzer. A heating rate of 10° min^{-1} with a 0.5 l min^{-1} purge of dry nitrogen was used in the TG and DTA runs.

RESULTS AND DISCUSSION

Tables 1 and 2 list the values of the equilibrium decomposition pressures, P(kPa), at the different temperatures for the IBN–$CoBr_2$ system and the

TABLE 1

Equilibrium decomposition vapor pressures at different temperatures for the IBN–$CoBr_2$ system containing the molar ratio $r = n(\mathrm{IBN})/n(\mathrm{CoBr_2})$

T(K)	P(kPa)	T(K)	P(kPa)	T(K)	P(kPa)
$r = 3.00$		$r = 2.32$		$r = 1.09$	
301.96	1.219	311.54	2.723	308.11	0.818
304.47	1.456	314.40	3.462	311.93	1.025
307.70	1.865	327.59	7.291	314.06	1.127
309.67	2.262	$r = 1.57$		316.35	1.289
309.77	2.308	305.57	0.695	323.03	1.840
312.25	2.849	309.89	0.813	333.25	3.038
315.05	3.497	313.45	1.091	337.04	3.527
318.95	4.624	314.40	1.044	338.98	4.011
333.84	10.518	318.13	1.380	343.66	4.742
$r = 2.57$		319.22	1.452	$r = 0.77$	
309.17	2.179	324.01	1.940	316.24	0.423
316.27	3.997	327.47	2.254	319.01	0.531
319.54	4.758	327.60	2.386	327.25	0.825
$r = 2.50$		333.03	3.226	328.12	0.870
307.97	1.947	336.48	3.778	333.46	1.156
312.13	2.709	339.18	4.388	342.58	1.908
317.12	4.165	340.11	4.605		
321.16	5.496				
322.98	5.922				
326.54	6.934				
326.78	7.131				
333.20	9.699				
344.14	14.797				
349.13	18.797				

TABLE 2

Equilibrium decomposition vapor pressures at different temperatures for the BCN–$CoBr_2$ system containing the molar ratio $r = n(\mathrm{BCN})/n(\mathrm{CoBr_2})$

T(K)	P(kPa)	T(K)	P(kPa)	T(K)	P(kPa)
$r = 1.83$		$r = 0.98$		$r = 0.28$	
319.18	0.373	325.05	0.593	319.18	0.373
321.07	0.400	326.80	0.627	326.63	0.647
326.63	0.633	329.32	0.752	326.80	0.627
326.80	0.600	332.07	0.883	332.80	0.880
332.80	0.920	332.80	0.960	334.47	1.035
334.47	1.047	334.47	0.995	338.35	1.280
338.35	1.253	335.68	1.047	342.91	1.773
342.91	1.840	338.35	1.253	344.70	1.907
344.70	2.000	342.91	1.687	348.32	2.346
348.32	2.380	344.70	1.913		
		348.32	2.260		

$BCN-CoBr_2$ system, respectively. Figure 1 shows plots of the logarithm of the decomposition pressure vs. $1/T$ for the different phases in the $IBN-CoBr_2$ system taken from the data in Table 1. Figure 2 is a similar plot for the $BCN-CoBr_2$ system taken from the data in Table 2. Also shown in these figures are plots of the logarithms of the vapor pressures of the corresponding liquid nitriles over the same temperature range [8].

As can be seen from Fig. 2, the $BCN-CoBr_2$ system is quite simple. The only stable phases in the temperature range studied are $Co(BCN)_2Br_2$ and $CoBr_2$. No evidence was found for a stable $Co(BCN)_3Br_2$ or $Co(BCN)Br_2$ phase. By extrapolation, the $Co(BCN)_2Br_2$ complex is stable up to 367 K where it would decompose to give $CoBr_2$ and liquid BCN. Table 3 lists the values of the thermodynamic parameters, ΔH^0 and ΔS^0, for the decomposition of $Co(BCN)_2Br_2$. In this table the ΔS^0 values are the standard entropy changes over the temperature ranges studied, corrected to a decomposition pressure of 1 atm. DTA and TG results were all consistent with the existence of only stable $Co(BCN)_2Br_2$.

The $IBN-CoBr_2$ system is more complex. Figure 3 shows a plot of the logarithm of the equilibrium decomposition pressure vs. the $IBN/CoBr_2$ molar ratio at 313 K. This isotherm indicates that three stable complexes exist: $Co(IBN)_3Br_2$, $Co(IBN)_2Br_2$ and $Co(IBN)Br_2$. Figure 1 also indicates only three stable complexes.

The $Co(IBN)_3Br_2$ complex is stable up to a temperature of about 318 K

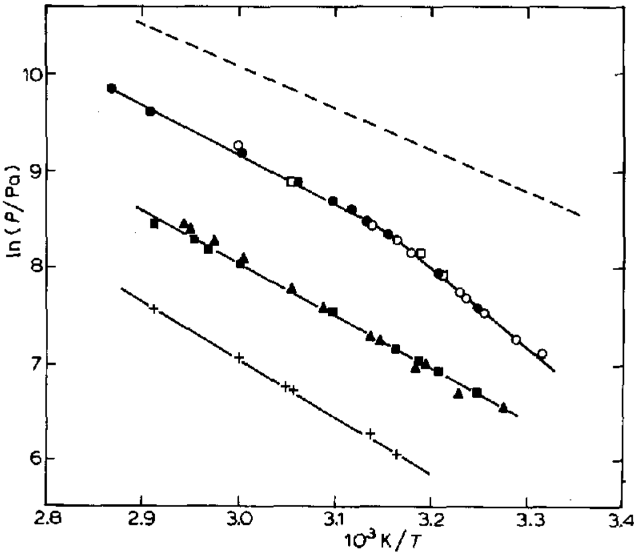

Fig. 1. Plot of equilibrium values of ln(P/Pa) vs. reciprocal temperature for the phase regions in the $IBN-CoBr_2$ system containing the molar ratio $r = n(IBN)/nCoBr_2$. Values of r are: ○, 3.00; ●, 2.57; •, 2.50; □, 2.32; ▲, 1.57; ■, 1.09; +, 0.77. The broken line represents the plot of the corresponding liquid nitrile.

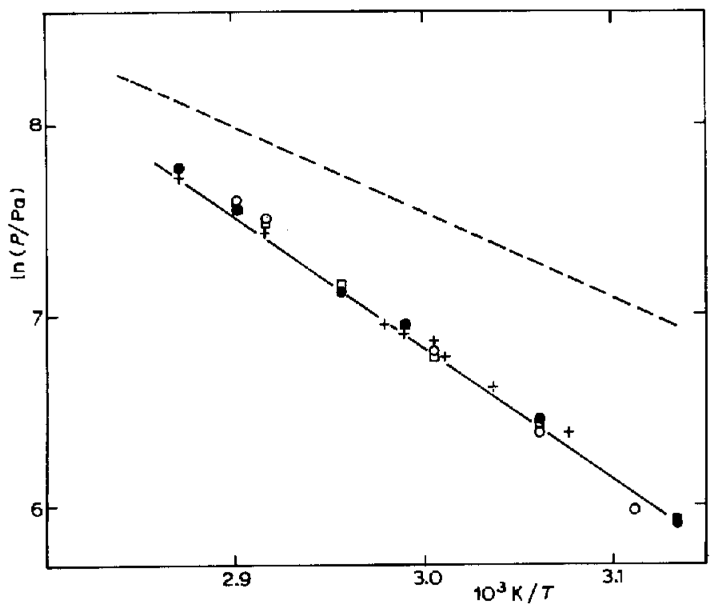

Fig. 2. Plot of equilibrium values of ln(P/Pa) vs. reciprocal temperature for the BCN–$CoBr_2$ system containing the molar ratio $r = n(BCN)/n(CoBr_2)$. Values of r are: ○, 1.83; +, 0.98; □, 0.28. The broken line represents the plot of the corresponding liquid nitrile.

where it either melts or decomposes to a saturated solution of some lower complex, presumably $Co(IBN)_2Br_2$, in liquid IBN. The ln P vs. 1/T plot for the melt yielded a value of ΔH^0 of 41.1 ± 1 kJ mole^{-1} and a ΔS^0 value of

TABLE 3

Standard enthalpy and entropy changes for the decomposition of cobalt(II) bromide–nitrile systems

Decomposition	ΔH^0 [a] (kJ mole^{-1})	ΔS^0 [a] (mole^{-1} K^{-1})
$Co(CH_3CN)_3Br_2(s) \rightarrow Co(CH_3CN)_2Br_2(s)+CH_3CN(g)$ [b]	49.8±0.5	144.6±1.7
$\frac{1}{2}$ $Co(CH_3CN)_2Br_2(s) \rightarrow \frac{1}{2}$ $CoBr_2(s)+CH_3CN(g)$ [b]	56.9±0.3	128.2±0.8
$Co(C_2H_5CN)_3Br_2(s) \rightarrow Co(C_2H_5CN)_2Br_2(s)+C_2H_5CN(g)$ [b]	55.7±0.4	150.4±1.2
$\frac{1}{2}$ $Co(C_2H_5CN)_2Br_2(s) \rightarrow \frac{1}{2}$ $CoBr_2(s)+C_2H_5CN(g)$ [b]	55.0±0.4	129.8±1.3
$Co(IBN)_3Br_2(s) \rightarrow Co(IBN)_2Br_2(s)+IBN(g)$ [c]	64.9±1.0	178.0±3.3
$Co(IBN)_2Br_2(s) \rightarrow Co(IBN)Br_2(s)+IBN(g)$	46.4±0.7	114.3±2.3
$Co(IBN)Br_2(s) \rightarrow CoBr_2(s)+IBN(g)$	50.5±0.7	114.3±2.3
$\frac{1}{2}$ $Co(BCN)_2Br_2(s) \rightarrow \frac{1}{2}$ $CoBr_2(s)+BCN(g)$	57.7±0.7	134.5±2.2

[a] Indeterminations are standard deviations.

[b] From ref. 5.

[c] Below 318 K.

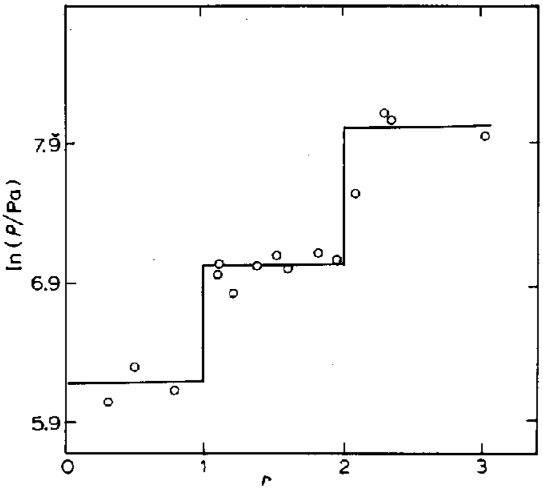

Fig. 3. Plot of equilibrium values of ln(P/Pa) vs. molar ratio $r = n(\mathrm{IBN})/n(\mathrm{CoBr_2})$ for the IBN–$CoBr_2$ system.

103.5 ± 2.8 J $\mathrm{mole^{-1}\ K^{-1}}$. Over this same temperature range the thermodynamic parameters for the vaporization of pure IBN are $\Delta H^0 = 35.9 \pm 0.3$ kJ $\mathrm{mole^{-1}}$ and $\Delta S^0 = (95.3 \pm 0.1)$ J $\mathrm{mole^{-1}\ K^{-1}}$ [8(b)]. The values of ΔH^0 are such that they cannot be used to argue for either a melting or a decomposition to a saturated solution.

The $Co(IBN)_2Br_2$ complex was stable up to the highest temperatures studied. By extrapolation, the complex would achieve a vapor pressure of 1 atm at 421 K. The $Co(IBN)_2Br_2$ has a lower limit of stability of 273.5 K where it would disproportionate to give $Co(IBN)_3Br_2$ and $Co(IBN)Br_2$. By extrapolation, it is estimated that $Co(IBN)Br_2$ would achieve a vapor pressure of 1 atm at approximately 442 K. For these lower complexes of IBN, equilibrium times are very slow (1 to 2 weeks) indicating kinetically slow reactions or slow diffusion of the nitrile through the solid.

The IBN–$CoBr_2$ system was also studied using DTA and TG. Because of the slow kinetics involved, it is difficult to correlate directly TG and DTA results with vapor pressure data. The DTA curves of samples with IBN/$CoBr_2$ mole ratios greater than two show an endotherm beginning at 318 K and reaching a maximum at 324 K corresponding to the 318 K decomposition of $Co(IBN)_3Br_2$. The DTA curves in the higher temperature region are more complex consisting of a series of irregularly shaped endotherms in the 433 to 458 K region that showed considerable variation in shape and peak temperatures as a function of heating rate. These peaks are the result of the superposition of endotherms corresponding to the boiling of the saturated solution or melt at about 398 K and the slow decompositions of $Co(IBN)_2Br_2$ and $Co(IBN)Br_2$ that are estimated to occur at 421 and

442 K, respectively. The DTA curves for samples with IBN/CoBr$_2$ molar ratios of one or below give a single broad endotherm centered at about 450 K, consistent with the predicted decomposition temperature of 442 K for Co(IBN)Br$_2$. Because of the overlapping of peaks, no quantitative DTA was undertaken. All that can be said is that DTA results are generally consistent with those predicted from extrapolation of the vapor pressure data.

Complications also arise in the interpretation of TG results. The TG curves show a number of ill-defined plateaus corresponding to fractional stoichiometries for the IBN–CoBr$_2$ system, whereas, vapor pressure results, such as those shown in Fig. 3, indicate only three stable stoichiometric compounds, Co(IBN)$_3$Br$_2$, Co(IBN)$_2$Br$_2$ and Co(IBN)Br$_2$. If the decomposition kinetics are slow and intermediate compounds are formed, dynamic methods such as TG could lead to misleading results in that metastable phases that are slow to decompose would be indistinguishable from thermodynamically stable phases. These same types of difficulties were found in the interpretation of thermal analysis results for the CH$_3$CN–NiCl$_2$ system which is also kinetically slow [4].

Table 3 lists the values of ΔH^0 and ΔS^0 for the decomposition of the different phases in the IBN–CoBr$_2$ and BCN–CoBr$_2$ systems along with values for some related systems. From the thermodynamic parameters listed in this table the values of ΔH^0 per mole of CoBr$_2$ can be calculated for the process

$$\mathrm{Co(RCN)_3Br_2(s)} \rightarrow \mathrm{CoBr_2(s)} + 3\ \mathrm{RCN(g)} \tag{1}$$

The values are: R = CH$_3$, 163.6 kJ mole^{-1}; R = CH$_3$CH$_2$, 165.7 kJ mole^{-1}; R = (CH$_3$)$_2$CH, 161.8 kJ mole^{-1}. These values are all quite close to one another and show no systematic trend with increasing size of the R group. Since the molar heats of vaporization, $\Delta H^0_{\mathrm{vap}}$, influence the values of ΔH^0 for eqn. (1) and vary from one nitrile to another, a better gauge of the relative stabilities of the Co(RCN)$_3$Br$_2$ complexes would be a comparison of the values of ΔH^0 for the process

$$\mathrm{Co(RCN)_3Br_2(s)} \rightarrow \mathrm{CoBr_2(s)} + 3\ \mathrm{RCN(liq)} \tag{2}$$

The reported values of $\Delta H^0_{\mathrm{vap}}$ for the nitriles used are: CH$_3$CN, 33.2 kJ mole^{-1} [9]; CH$_3$CN$_2$CN, 36.8 kJ mole^{-1} [10]; (CH$_3$)$_2$CHCN, 36.8 kJ mole^{-1} [8(b)]. Using these values, the values of ΔH^0 per mole of CoBr$_2$ for eqn. (2) can be estimated to be 64.0 kJ mole^{-1} for R = CH$_3$, 58.3 kJ mole^{-1} for R = CH$_3$CH$_2$ and 51.4 kJ mole^{-1} for R = (CH$_3$)$_2$CH. These values show a slight, systematic decrease with increasing CH$_3$ substitution on the C adjacent to the CN group. This same downward trend is seen for the ΔH^0 values for the decomposition of the corresponding Co(RCN)$_2$Br$_2$(s) to CoBr$_2$(s), and either gaseous or liquid RCN. This trend, although small, could be rationalized in terms of increased steric hindrance of the alkane affecting the

CN–Co bond. However, this contribution must be very small since IR evidence indicates that one nitrile in the $Co(CH_3CN)_3Br_2$ complex is uncoordinated, whereas all nitriles in the other $Co(RCN)_3Br_2$ complexes are bonded. The slight decrease in stability shown in these complexes is more likely due to increased steric interactions destabilizing the crystal structure rather than affecting the CN–Co bond strength. Consistent with this is the report by Zuur et al. [11] that neither the crystal field parameters, Dq and B, nor the shifts in the C≡N stretching frequencies showed any variations in the series of complexes $[Co(RCN)_6][SbCl_6]_2$ for R=CH_3, n-C_3H_7, $(CH_3)_2CH$, C_6H_5 and $(CH_3)_3C$. Both the crystal field parameters and the $\nu_{C\equiv N}$ shift should be sensitive to the CN–Co interaction. In addition, the fact that, even though IR evidence indicates that one of three nitriles in $Co(CH_3CN)_3Cl_2$ is uncoordinated, the values of ΔH^0 for the removal of the first two nitriles are the same within experimental error, points to the dominance of crystal packing forces in determining the decomposition thermodynamics for these systems.

Crystal packing forces can also be used to account for the change in the maximum nitrile to metal halide molar ratios with increasing chain length of the alkyl group of the nitrile. For the RCN–$CoBr_2$ systems, CH_3CN, C_2H_5CN and $(CH_3)_2CHCN$ form stable three complexes, the highest complex with n-C_3H_7CN is a two complex and n-C_4H_9CN forms only the one complex [12]. For the RCN-$CoCl_2$ systems, CH_3CN forms a stable $Co(CH_3CN)_3Cl_2$ while the highest stoichiometry with C_2H_5CN is $Co(C_2H_5CN)_2Cl_2$ [13]. As the alkyl group on the nitrile is extended farther out in space by increasing the chain length, steric repulsion between the large cations will prevent formation of the highest complexed cation giving rise to

TABLE 4

Standard enthalpies of formation at 25°C, ΔH_f^0, for nitrile–cobalt(II) halide complexes

Complex	ΔH_f^0 (kJ mole^{-1})
$Co(CH_3CN)_3Cl_2(s)$	−269.9 [a]
$Co(CH_3CN)_2Cl_2(s)$	−288.4 [a]
$Co(CH_3CN)Cl_2(s)$	−307.0 [a]
$Co(CH_3CN)_3Br_2(s)$	−186.8 [a]
$Co(CH_3CN)_2Br_2(s)$	−202.9 [a]
$Co(C_2H_5CN)_3Br_2(s)$	−232.1 [a]
$Co(C_2H_5CN)_2Br_2(s)$	−227.9 [a]
$Co[(CH_3)_2CHCN]_3Br_2(s)$	−321.3
$Co[(CH_3)_2CHCN]_2Br_2(s)$	−272.1
$Co[(CH_3)_2CHCN]Br_2(s)$	−248.6
$Co(n\text{-}C_3H_7CN)_2Br_2(s)$	−273.5

[a] From data in ref. 3.

lower coordintion of the metal ion by nitrile molecules. The larger bromide ion should serve to mediate this steric repulsion better than chloride, thus enabling higher coordination of larger nitriles to exist in the RCN–$CoBr_2$ system than in the RCN–$CoCl_2$ system.

Table 4 lists the values of ΔH_f^0 of the compounds in the nitrile–cobalt halide systems at 298 K. The ΔH_f^0 values for the $Co(RCN)_yX_2$ complexes were calculated using the ΔH^0 values listed in Table 3 and reported values of ΔH_f^0 for the respective nitriles [14] and cobalt halides [15]. When CH_3CN is the ligand, the ΔH_f^0 values become more negative as the nitrile content decreases; when C_2H_5CN is the ligand, the ΔH_f^0 values do not vary much with nitrile content and for IBN, the ΔH_f^0 values become less negative with increasing nitrile content. These variations, which are in the opposite direction from the variations in the ΔH^0 values for eqn. (2), reflect the changes in the values of ΔH_f^0 for the different nitrile molecules rather than the relative stabilities of the complexes themselves.

REFERENCES

1 B.N. Storhoff and H.L. Lewis, Jr., Coord. Chem. Rev., 23 (1977) 1 and references therein.
2 B.J. Hathaway and G.H. Holah, J. Chem. Soc., (1964) 2400.
3 J.A. Maguire, J.J. Banewicz and C.L. Ragan, J. Chem. Thermodyn., 8 (1977) 821.
4 J.J. Banewicz, J.A. Maguire, M.E. Munnell and M.L. Moore, Thermochim. Acta, 12 (1975) 377.
5 J.J. Banewicz, J.A. Maguire, P.O. Smith, D. Lussky, D.W. Sudbrink and D.E. Allen, J. Chem. Thermodyn., 13 (1981) 629.
6 G. Beech, G. Marr and S.J. Ashcroft, J. Chem. Soc., (1970) 2903.
7 Natl. Bur. Stand. (U.S.) Monogr., 8 (1961).
8 (a) E.F. Meyer and R.D. Holtz, J. Chem. Eng. Data, 18 (1973) 359. (b) J.A. Maguire and J.J. Banewicz, to be published.
9 W.E. Putman, D.M. McEachern, Jr. and J.E. Kilpatrick, J. Chem. Phys., 42 (1965) 759.
10 L.A. Weber and J.E. Kilpatrick, J. Chem. Phys., 36 (1962) 829.
11 A.P. Zuur, A.H.L. Reintjis and W.L. Groeneveld, Recl. Trav. Chim. Pays-Bas, 89 (1970) 385.
12 D.E. Welsh, M.S. Thesis, Southern Methodist University, 1982.
13 J.A. Maguire, J.J. Banewicz and E. O'Sullivan, unpublished results.
14 H.K. Hall, Jr. and J.H. Boldt, J. Am. Chem. Soc., 93 (1971) 140.
15 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and W.H. Schumm, Natl. Bur. Stand. (U.S.) Tech. Note, 270-4 (1969).