1111. *The Relative Stabilities of Halogeno-complexes. Part IV.*[1] *The* trans-Rh en$_2$Cl$_2$$^+$–Br$^-$ *Equilibria*

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Equilibrium constants for the successive replacement of chloride in *trans*-Rh en$_2$Cl$_2$$^+$ by bromide have been obtained spectrophotometically. $K_1 = 1{\cdot}9_5$ and $K_2 = 0{\cdot}8$, at 85° and an ionic strength of 1·5M; 95% confidence limits are about ±0·2 and ±0·1, respectively. The enthalpy change for the overall replacement is close to zero. The five-co-ordinate unit (Rh en$_2$X)$^+$ becomes more class (b) when X is changed from chloride to bromide, and the lower class (b) character of the rhodium(III) system compared with the analogous platinum(IV) system is ascribed largely to bond-strength effects.

The equilibrium constants for successive replacement of chloride in *trans*-Rh en$_2$Cl$_2$$^+$ by bromide have been measured spectrophotometrically in order to obtain a measure both of the class (a) or (b) character of rhodium(III) in these complexes [2] and of the relative thermodynamic effects which chloride and bromide transmit across the metal ion. The dichloro-complex was dissolved in 1·5M-potassium halide solutions having various chloride : bromide ratios and allowed to come to equilibrium. The equilibrium constants were then estimated from ultraviolet absorption spectra.

Results

Ultraviolet and Visible Absorption Spectra.—The principal features of the absorption spectra of the dichloro- and dibromo-complexes are recorded in Table 1 together with those previously reported [3] and those for the new bromochloro-complex. The agreement with published work is good for the dichloro-complex, but higher extinction coefficients were repeatedly obtained for the dibromocomplex.

Although Johnson and Basolo obtained a satisfactory analysis for their dibromo-compound their preparation involved refluxing of the dichloro-complex for only 45 minutes with bromide. A knowledge of the kinetics of this reaction [4] suggests that it cannot have been complete under these conditions, and this may explain the lower extinction coefficients which they obtained.

Table 1

Absorption spectra of *trans*-Rh en$_2$XY$^+$ complexes

	λ (mμ)		ε (cm.$^{-1}$ l. mole^{-1})	
	This work	Ref. 3	This work	Ref. 3
X = Y = Cl	407, 286	406, 286	75, 125	75, 130
X = Br, Y = Cl ...	486sh, 413, 262sh	—	~10, 95, ~1600	—
X = Y = Br	425, 276, 231	425, 276, —	120, 3000, ~31,000	100, 1800, —

The spectrum of the bromochloro-complex is intermediate between those of the *trans*-dichloro- and *trans*-dibromo-complexes. This suggests that the bromochloro-complex also has a *trans* configuration. No *trans* ⟶ *cis* geometrical isomerisation has been observed in any reactions of these rhodium(III) complexes,[3,5] and the bromochloro-complex reacts with chloride and bromide to give the *trans*-dichloro- and *trans*-dibromo-complex, respectively.

The trans-Rh en$_2$Cl$_2$$^+$–Br$^-$ *Equilibria.*—Solutions of the complex in chloride–bromide mixtures were made up so as to give final absorbances of up to 1 or 1·5 units at 276 mμ. They were allowed to come to equilibrium at 85° or 95°, a process which lasted about 3 days and 1

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[1] Part III, A. J. Poë, *J.*, 1963, 183.

[2] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[3] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925.

[4] F. Basolo, E. J. Bounsall, and A. J. Poë, *Proc. Chem. Soc.*, 1963, 366.

[5] (*a*) R. Klabunde and F. Basolo, personal communication; (*b*) E. J. Bounsall, personal communication.

day, respectively. The relationship between the apparent extinction coefficient (ε) of the solution, the extinction coefficients of the dichloro-(ε_0), bromochloro- (ε_1), and dibromo-complexes (ε_2), the equilibrium constants K_1 and K_2 for the replacement of the first and second chloride ions, respectively, and the [Br$^-$]/[Cl$^-$] ratios (R) is expressed by the equation:

$$(\varepsilon - \varepsilon_0) + (\varepsilon - \varepsilon_1)RK_1 + (\varepsilon - \varepsilon_2)R^2K_1K_2 = 0 \qquad (1)$$

The total concentration of each halide ion was always sufficiently large for any losses or gains during adjustment to equilibrium to be negligible. Preliminary values of K_1 and K_2 were obtained from the gradient and intercept of a plot of $(\varepsilon - \varepsilon_0)/R^2(\varepsilon_2 - \varepsilon)$ against $(\varepsilon_1 - \varepsilon)/R(\varepsilon_2 - \varepsilon)$. The product K_1K_2 was calculated from equation (1) by inserting the approximate value of K_1, obtained graphically, and each of the experimental values of ε. The average value of K_1K_2 so obtained was then used to calculate K_1 from equation (1). When ε was close to ε_1 the values calculated for K_1 were inherently inaccurate and were not included. K_1K_2 was then recalculated by using the new value of K_1, and this process was continued until no further changes in the constants were obtained. The experimental data, from two sets of solutions, and the final set of constants are shown in Table 2. The errors quoted are 95% confidence limits based on the standard deviations of the sets of values. Systematic errors due to 5% uncertainties in the extinction coefficients are about the same so final values of K_1 and K_2 can be taken as $1{\cdot}9_5 \pm 0{\cdot}2$ and $0{\cdot}8 \pm 0{\cdot}1$, respectively, with about 95% confidence. Data obtained at 95° are so close to those obtained at 85° that the enthalpy changes involved in the reactions must be within about 1 kcal./mole of zero.

Constants obtained by using data at 262 mμ were in reasonable agreement with those quoted above, and such differences as there were could be ascribed to the presence of small amounts of decomposition products absorbing more strongly at 262 than at 276 mμ.

TABLE 2

Calculation of K_1 and K_2 from data at 276 mμ; $\mu = 1{\cdot}5$M, $T = 85°$ ($\varepsilon_0 = 100$, $\varepsilon_1 = 1150$, and $\varepsilon_2 = 3000$ cm.$^{-1}$ l. mole^{-1})

R	ε	$(\varepsilon - \varepsilon_0)$	$(\varepsilon - \varepsilon_1)R$	$(\varepsilon_2 - \varepsilon)R^2$	K_1K_2 $(K_1 = 1{\cdot}90)$	K_1 $(K_1K_2 = 1{\cdot}58)$
0·250	586	486	−141	150	1·45	1·77
0·250	581	481	−143	151	1·39	1·61
0·286	683	583	−134	192	1·72	2·09
0·286	641	541	−146	195	1·35	1·60
0·333	795	695	−118	246	1·92	2·60
0·333	749	649	−133	250	1·60	1·91
0·400	860	760	−116	342	1·58	—
0·400	851	751	−120	344	1·52	—
0·500	1037	937	−56	490	1·70	—
0·500	998	898	−75	500	1·51	—
0·667	1172	1072	+15	810	1·36	—
0·667	1247	1147	64	725	1·75	—
1·00	1563	1463	413	1440	1·56	1·96
1·00	1514	1414	364	1490	1·41	2·58
1·32	1780	1679	825	2100	1·55	2·10
1·32	1827	1727	890	2040	1·65	1·78
1·61	1972	1872	1330	2660	1·65	1·82
1·61	1966	1866	1320	2680	1·64	1·86
1·92	2104	2004	1830	3340	1·64	1·77
1·92	2098	1998	1820	3330	1·64	1·78

Averages: $K_1K_2 = 1{\cdot}58 \pm 0{\cdot}06$; $K_1 = 1{\cdot}95 \pm 0{\cdot}16$; $K_2 = 0{\cdot}81 \pm 0{\cdot}07$.

DISCUSSION

The values of the constants show that this rhodium(III) system is on the border between class (a) and class (b). This would be expected on the basis of other data discussed by Ahrland, Chatt, and Davies.[2] The overall constant (K_1K_2) for the system is 1·6, indicating slight overall class (b) character, but the values of K_1 and K_2 appear to show that the first stage is slightly class (b), and the second slightly class (a). Allowance for statistical effects, however, leads to intrinsic or chemical constants [6] $K_1' = 0{\cdot}9_7 \pm 0{\cdot}1$ and $K_2' = 1{\cdot}6 \pm 0{\cdot}2$, and these are a more truly chemical measure of the relative ease of replacement of chloride by bromide in each step. The first replacement is therefore exactly on the borderline and the second is slightly class (b). This is consistent with the views of Pearson,[7] who classifies Lewis acids and bases as " soft " or " hard," the degrees of softness being related to the polarisability, and who concludes that, in general, hard acids tend to react more completely with hard bases and soft acids with soft bases. In our case, the five-co-ordinate Lewis acid $(\mathrm{Rh\,en_2X})^+$ is more soft when $\mathrm{X = Br^-}$ than when $\mathrm{X = Cl^-}$, as shown by the relatively greater preference of $(\mathrm{Rh\,en_2Br})^+$ for the softer base $\mathrm{Br^-}$. The ligand X therefore transmits a small but definite effect across the metal ion. In the absence of comparable data on corresponding *cis*-complexes, it is not clear whether this effect is specifically a *trans* effect or not. The transmitted effect is very close to that in the *trans*-$\mathrm{Pt\,en_2Cl_2{}^{2+}}$–$\mathrm{Br^-}$ system,[1] which is surprising in view of the greater effective charge and consequent lower polarisability expected for the platinum(IV) ion.

The overall class (b) character is less than that of the $\mathrm{Pt\,en_2Cl_2{}^{2+}}$–$\mathrm{Br^-}$ system for which the overall constant (at ~20°) is 49. Platinum(IV) would be expected to be less class (b), or less " soft," than rhodium(III) in view of its lower polarisability. In addition, the larger charge on the platinum(IV) complex might be expected to lead to a greater loss of hydration energy when the complex ion changes from the dichloro- to the larger dibromo-form.[8] This would also lead to a smaller class (b) character. The greater absolute bond strength in the platinum(IV) complex, caused by the higher effective ionic charge, might also be expected to lead to a larger difference in the strengths of the M–Cl and M–Br bond, and so to a smaller class (b) character.[8] However, simple calculations [9] based on an ionic model [10] involving linear X–M–X units show that between effective ionic charges $Z^* = 3{\cdot}5$ and $Z^* = 5$ the bond-strength difference can actually decrease owing to the increasing importance of charge–induced-dipole interactions. These are larger for the M–Br bond owing to the greater polarisability of the bromide ion. If the M–Cl bond length is 2·5 Å and the M–Br bond is 0·15 Å longer, the bond strength difference decreases from 9 to 4 kcal./mole on increasing Z^* from 3·5 to 5. The extent of this decrease is not very sensitive to small variations in the bond length parameters. It is larger than the difference in class (b) character as expected since it has to overcome the solvation effects. Although the ionic model is capable of indicating a probable explanation for the relatively large difference in the class (b) character of the rhodium(III) and platinum(IV) systems it is not successful in explaining the much smaller transmitted effects which are observed. These arguments are strictly only appropriate to a classification based on enthalpy data but these are not yet available for the platinum(IV) system.

Since the equilibrium constant data at 85° and 95° were indistinguishable, $\Delta H_1°$ and $\Delta H_2°$ must certainly be within about 1 kcal./mole of zero. The replacement of bromide by chloride as the free anion in solution leads to a decrease of 8·12 kcal./mole in the enthalpy of the system,[11] so the change in the complex from $(\mathrm{Rh\,en_2XCl})^+$ to $(\mathrm{Rh\,en_2XBr})^+$ involves an increase in enthalpy of about the same amount. Although a part of this 8 kcal./mole increase is presumably due to the lesser solvation of the larger bromo-complex, the major part can be attributed to the smaller strength of the Rh–Br bond.[8] This value is larger than those found for the few cases of hexa- or tetra-halogeno-complexes for which data are available.[8] This can be explained by the greater ligand–ligand repulsion terms in the anionic complexes. These have a smaller unfavourable effect on the bromo-complexes, in which the anionic ligands are farther apart.

[6] S. W. Benson, *J. Amer. Chem. Soc.*, 1958, **80**, 5151.
[7] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; " Proceedings of the 8th International Conference on Co-ordination Chemistry," Springer-Verlag, Vienna, 1964, p. 315.
[8] A. J. Poë and M. S. Vaidya, *J.*, 1961, 1023.
[9] H. L. Bott, unpublished work.
[10] F. J. Garrick, *Trans. Faraday Soc.*, 1932, **14**, 914.
[11] L. Benjamin and V. Gold, *Trans. Faraday Soc.*, 1954, **50**, 797.

EXPERIMENTAL

The complex ion Rh $en_2Cl_2^+$ was prepared as previously described,[3] and isolated as the perchlorate. The purity was judged by the identity of the visible and ultraviolet absorption spectra with those of Johnson and Basolo.[3] The dibromo-complex was obtained by refluxing the dichloro-complex with a large excess of sodium bromide in slightly acid solution for about 4 hr. This product was also isolated as the perchlorate, which was recrystallised several times from slightly acid bromide solutions (Found: C, 10·4; H, 3·3; Br + Cl, 41·8, 42·0, 40·3; N, 10·4. Calc. for $C_4H_{16}BrCl_2N_4O_4Rh$: C, 10·0; H, 3·3; Br + Cl, 40·5; N, 11·6%).

trans-*Bisethylenediaminebromochlororhodium*(III) *perchlorate* was prepared either by the anation of the chloroaquocomplex with bromide or by the anation of the bromoaquo-ion with chloride. The bromoaquo-complex was prepared *in situ* by refluxing an aqueous solution of the dibromo-complex (1 g. in 50 ml.) with 1 equivalent of silver nitrate (0·36 g.) for about 2 hr., after which no further change in the aborption spectra occurred. The precipitated silver bromide was removed by filtration. Anation with a twenty-fold excess of concentrated hydrochloric acid was continued until no further changes were observed in the absorption spectra of suitably diluted reaction mixtures. The complex was isolated as the perchlorate or the nitrate by addition of ice-cold concentrated acid (10 ml.) to the cooled reaction mixture. The resulting precipitate was redissolved in a minimum of warm water and reprecipitated by cooling the solution and adding concentrated acid. The preparation from the dichloro-complex was carried out similarly but gave products with less reproducible absorption spectra and less good analyses. This is probably because the reaction of Rh en_2BrCl^+ with Cl^- to give Rh $en_2Cl_2^+$ is considerably slower than that of Rh en_2BrCl^+ with Br^- to give Rh $en_2Br_2^+$.[12] Analyses of *perchlorates* and *nitrates* prepared from the dibromo-complex were, respectively, as follows. Found: C, 11·3; H, 3·4; Cl + Br, 34·5; N, 12·3. $C_4H_{16}BrCl_2N_4O_4Rh$ requires C, 10·9; H, 3·6; Cl + Br, 34·5; N, 12·8%. Found: C, 12·4; H, 3·4; Cl + Br, 29·2; N, 18·9. $C_4H_{16}BrClN_5O_3Rh$ requires C, 12·0; H, 4·0; Cl + Br, 28·8; N, 17·5%.

Solutions for equilibrium studies were made up as outlined above by making use of AnalaR potassium halides which had been finely powdered and dried. The solutions were kept at 85 or 95° in an oil bath controlled to within ±0·05°. At regular time intervals aliquots of the solutions were rapidly cooled to room temperature and their spectra recorded with a Perkin-Elmer (model 350) recording spectrophotometer. The reactions of these complexes are sufficiently slow [4,12] for no readjustment of the equilibria to have occurred between removal of the solutions from the bath and measurement of their spectra. When successive spectra of the same solutions were identical, the solutions were taken to be at equilibrium. Care was needed in this respect since the solution underwent slow subsequent decomposition to unidentified products. At 70° the decomposition reaction overlapped with the establishment of equilibrium to such an extent that accurate values of the equilibrium constants were unobtainable.

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[12] H. L. Bott and A. J. Poë, unpublished results.