

References and Notes

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- (2) W. Fink, *Angew. Chem.*, **78**, 803 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 760 (1966).
- (3) K. Lienhard and E. G. Rochow, *Z. Anorg. Allg. Chem.*, **331**, 316 (1964).
- (4) K. A. Andrianov, V. N. Talanov, L. M. Khanashvili, N. P. Gashnikova, M. M. Il'in, and N. A. Sidorenko, *Dokl. Akad. Nauk SSSR*, **198**, 87 (1971).
- (5) K. A. Andrianov, G. V. Kotrelev, E. F. Tonkikh, and I. M. Ivanova, *Dokl. Akad. Nauk SSSR*, **201**, 349 (1971).
- (6) P. J. Wheatley, *J. Chem. Soc.*, 1721 (1962).
- (7) G. Chioccala and J. Daly, *J. Chem. Soc.*, 1658 (1968).
- (8) U. Wannagat, P. Schmidt, and M. Schulze, *Angew. Chem.*, **79**, 409 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 447 (1967).
- (9) P. G. Lenhart and D. Henry, "A Diffractometer Control Program", paper M8, Abstracts of the American Crystallographic Association Meeting, New Orleans, La., 1970.
- (10) P. J. Wehe, W. R. Busing, and H. A. Levy, ORABS, Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
- (11) P. T. Miller, P. G. Lenhart, and M. D. Joesten, *Inorg. Chem.*, **11**, 2221 (1972).
- (12) J. F. Stewart, F. A. Kundell, and J. C. Baldwin, "X-RAY 70 System of Crystallographic Programs", University of Maryland, College Park, Md., July 1970.
- (13) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (15) See paragraph at end of paper regarding supplementary material.
- (16) H. Gross-Ruyken and K. Schaarschmidt, *Chem. Tech., (Berlin)*, **11**, 451 (1959).
- (17) C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Studies of Propanediol–Chromium(III) Species in Acidic Solution¹

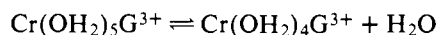
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Abstract: The reactions of $\text{Cr}(\text{OH}_2)_6^{3+}$ in acidic water–propanediol to form species $\text{Cr}(\text{OH}_2)_w\text{G}_g^{3+}$ (G = glycol) have been studied at 60 °C to allow comparison of the properties of systems in which the chelate rings contain five atoms (1,2-propanediol) and six atoms (1,3-propanediol). For 1,3-propanediol, species with $g = 1, 2,$ and 3 have been separated from equilibrated solutions by column ion-exchange procedures. Species containing a particular number of coordinated glycol molecules and different numbers of coordinated water molecules have been isolated, indicating that 1,3-propanediol bonds to chromium(III) ion as a chelated and as a nonchelated ligand. Equilibrium quotients for the reactions, which depend upon the solvent composition, have relative values close to statistical. For 1,2-propanediol, species with $g > 1$, if they form, do not survive the ion-exchange separation procedure. This system resembles the ethylene glycol system, and it is suggested that a 1,2-glycol chelated to chromium(III) labilizes the other coordination sites.

A recent study² of species of chromium(III) ion in acidic water–ethylene glycol mixed solvents reveals unexpected results. These are: (1) a relatively rapid spectral change which occurs when previously equilibrated solutions are diluted with a solvent component to alter the solvent composition, and (2) species containing two or more coordinated glycol molecules, as determined by ion-exchange procedures, are present, if at all, at much lower concentrations than expected statistically. This contrasts with the chromium(III) species involving coordinated alcohols³ and dimethyl sulfoxide,⁴ the relative stabilities of which are only moderately different from statistical.

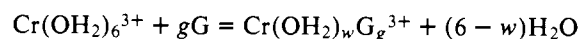
The relatively rapid spectral change occurring upon dilution was interpreted to be due to the shifting of equilibrium in the reaction



in which the coordinated glycol ligand, represented by G , acts as a monodentate reagent in $\text{Cr}(\text{OH}_2)_5\text{G}^{3+}$ and as a chelated bidentate reagent in $\text{Cr}(\text{OH}_2)_4\text{G}^{3+}$. The failure to isolate chromium(III) species containing two or more coordinated glycol molecules was not explained, although the possibility that such species were present at equilibrium but did not survive the ion-exchange procedure was mentioned. If the kinetic and equilibrium behavior of the chromium(III)–ethylene glycol system is attributable to specific properties of the five atom chelate ring in tetraqua(ethylene glycol)chromium(III) ion, study of chromium(III) coordinated to the isomeric propanediols should reveal differences between the species involving 1,2-propanediol (which would form five-atom chelate

rings) and those involving 1,3-propanediol (which would form six-atom chelate rings). The present paper deals with such a study, which reveals a remarkable contrast between these two systems.

The species which are possible in a system of six-coordinate chromium(III) and a ligand which can act as either a monodentate or a bidentate ligand, such as a glycol, have the composition $\text{Cr}(\text{OH}_2)_w\text{G}_g^{3+}$. The number of bidentate glycol ligands in this species is $6 - (w + g)$. Equilibrium in the solutions can be characterized by equilibrium quotients for the reactions forming each of these species from hexaaquachromium(III) ion:



with

$$Q_{gw} = \frac{[\text{Cr}(\text{OH}_2)_w\text{G}_g^{3+}](1 - Z)^{6-w}}{[\text{Cr}(\text{OH}_2)_6^{3+}]Z^g}$$

in which Z is the mole fraction of propanediol in the mixed solvent. (In calculation of Z , only the solvent components are taken into account.) For many compositions of chromium species (particular values of w and g), geometric and optical isomers are possible.

Experimental Details and Results

Reagents. Reagent grade chemicals were used without additional purification unless noted otherwise. The water content of the 1,2-propanediol (Fisher Scientific Co., Laboratory Grade) and 1,3-propanediol (Eastman Kodak, Reagent Grade) was determined by Karl Fischer titrations. Solutions of chromium(III) perchlorate in per-

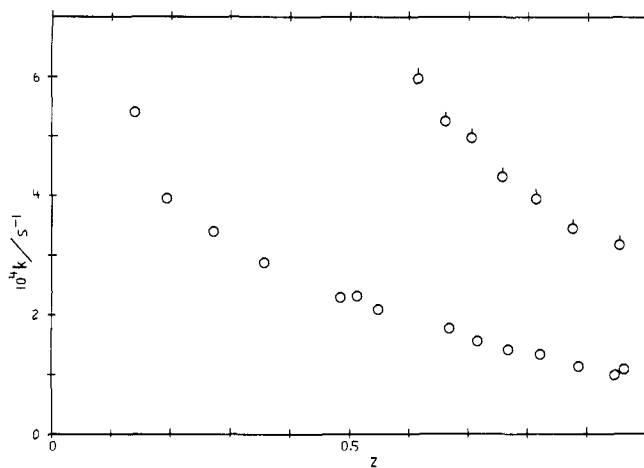


Figure 1. Values of the first-order rate constant for the approach to equilibrium, $k = d \ln(A_{t+\tau} - A_t)/dt$, as a function of solvent composition at 60 °C: upper curve \circ , 1,2-propanediol; lower curve \circ , 1,3-propanediol.

chloric acid were prepared as described previously.³ Dowex 50W-X8 (Baker Chemical Co.) ion exchange resin, used in the hydrogen ion form, was cleaned by rinsing with water, heating with alkaline hydrogen peroxide (~0.1 M NaOH, 0.01 M H₂O₂), treatment with acid (2 M HCl), and rinsing with distilled water until the rinse was neutral and free of chloride ion.

Analyses. In the evaluation of \bar{g} (the average number of glycol molecules coordinated to chromium(III)) by ion-exchange procedures, the chromium(III) content of portions of eluent was determined spectrophotometrically following oxidation to chromate ion in alkaline hydrogen peroxide.^{2,5} A more rapid, but less accurate, atomic absorption method was used to analyze for chromium in portions of eluent from long column ion exchange separations of the different chromium(III) species present in equilibrated aqueous solutions of 1,3-propanediol. This analytical procedure was calibrated with solutions of known concentrations of chromium having the same acidity as the portions of eluent. Its use was confined to a range of chromium concentration ($<1.5 \times 10^{-4}$ M) in which linearity of absorbance vs. concentration was observed. Analysis of propanediol was carried out by determination of the light absorption at 610 nm due to chromium(III) produced in the reduction of chromium(VI) by propanediol in concentrated sulfuric acid (10.5 M).^{2,6} This study confirms the observations of Sargent and Rieman⁶ that 1,2-propanediol is oxidized to a mixture of products. For 1,3-propanediol, the stoichiometry is within a few percent of that corresponding to complete oxidation to carbon dioxide. Each analysis was used, however, in a strictly empirical fashion based upon calibration with known amounts of propanediol analyzed in an identical manner. These analyses were accurate to $\pm 2\%$ (1,2-propanediol) and $\pm 0.5\%$ (1,3 propanediol).

The Kinetics of Approach to Equilibrium. The substitution of water in the coordination shell of chromium(III) with either isomeric propanediol results in an increase in light absorption. Measurement of absorbance as a function of time was used, therefore, to determine the rate of approach to equilibrium at 60 °C for each system. For the chromium(III)-1,2-propanediol system, measurements were made at 575 nm, and for the chromium(III)-1,3-propanediol system, measurements were made at several wavelengths in the range 450–620 nm. The approach to equilibrium was nicely first order in the chromium(III)-1,2-propanediol system, and this was approximately true for the chromium(III)-1,3-propanediol system. In the latter system, however, there was a slowly increasing absorption of light by the solvent. This was judged to be due to oxidation, which was spectrally detectable but stoichiometrically insignificant. Figure 1 gives values of the first-order rate constant for the approach to equilibrium ($k = d \ln(A_{t+\tau} - A_t)/dt$), determined by the Guggenheim method⁷ for each of these systems as a function of solvent composition.

Relatively rapid spectral changes do not occur when a previously equilibrated solution of chromium(III) in acidic aqueous 1,3-propanediol is diluted with aqueous acid. The chromium(III)-1,2-propanediol system behaves in this respect, however, just as the chromium(III)-ethylene glycol system,² and a relatively rapid decrease of light absorption occurs when solutions equilibrated at $Z = 0.96$ are diluted with aqueous acid to $Z \approx 0.3$ to $Z \approx 0.8$. This relatively rapid

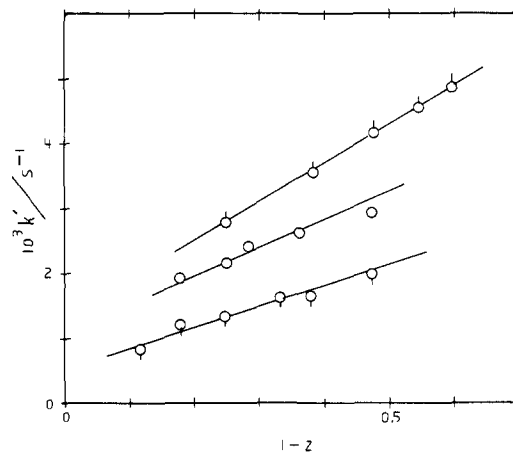


Figure 2. Values of k' ($k' = d \ln(A_t - A_{t+\tau})/dt$) vs. $(1 - Z)$, the mole fraction of water, for the change of light absorption at 575 nm, which occurs when a solution with $Z = 0.96$ is diluted with aqueous acid: \circ , 25 °C; \circ , 30 °C; \circ , 35 °C.

spectral change, measured at 575 nm, conforms closely to a first-order process. Values of the first-order rate constant, k' , for the approach to a new equilibrium upon dilution, evaluated using the Guggenheim procedure, are presented in Figure 2. The linear plots of k' vs. $(1 - Z)$, also observed in the chromium(III)-ethylene glycol system, are expected if the cause of the relatively rapid spectral change is monodentate-bidentate interconversion.

The approach to equilibrium in a solution with $Z = 0.703$ (1,2-propanediol) starting with hexaaquachromium(III) ion was studied as a function of temperature. These data for solutions with 0.099 M perchloric acid and 0.010 M chromium(III) perchlorate are (given as T (°C), $10^4 k$ (s⁻¹)) 40, 0.41; 55, 2.80; and 60, 4.98. The relatively rapid change which occurs when a solution of $Z = 0.96$ (1,2-propanediol) is diluted with aqueous acid also was studied as a function of temperature. For dilution to $Z = 0.53$, the values of k' as a function of temperature are (given as T (°C), $10^3 k'$ (s⁻¹)) 25, 2.00; 30, 2.93; and 35, 4.42 (average of two values).

Cation-Exchange Procedures. Two types of ion-exchange procedures were used in this study. In experiments designed to determine \bar{g} for each of the two systems, a portion of equilibrated solution was quenched in a large volume of cold (~0 °C) 0.1 M perchloric acid containing an amount of resin (100–200 mesh) which would take up all of the cationic chromium(III) species. This mixture was stirred at ~0 °C for 45 min, during which time the exchange of chromium(III) into the resin phase was complete. This loaded resin (~1.2 cm³) was rinsed with cold 0.02 M sulfuric acid and then added to a short column containing ~3 cm³ of resin where the rinsing was continued until the rinse was free of glycol. Elution with 3.0 M sulfuric acid (1,2-propanediol system) or 6.0 M sulfuric acid (1,3-propanediol system) results in essentially complete recovery of chromium(III). (Actual recovery will be presented in reporting the results.) The other type of ion-exchange procedure was used to separate individual species in the chromium(III)-1,3-propanediol system. In these experiments, a long, jacketed column (8 mm diameter \times 110 cm) was filled to a depth of 70–100 cm with resin (200–400 mesh). During the 5–9 days of elution, antifreeze at ~0 °C was circulated through the column's annular jacket.

Values of \bar{g} . Determination of the binding of propanediol by chromium(III) ion in acidic mixed solvents of water with the isomeric propanediols has been carried out by column ion-exchange procedures, already described. In earlier studies,^{3,4} it was assumed that aquation of various chromium(III)-alcohol³ or chromium(III)-dimethyl sulfoxide⁴ species does not occur to an appreciable extent in the ion-exchange procedures carried out at low temperature (~0 °C). Such an assumption allows the value of \bar{g} , so determined, to be identified as the value appropriate for the equilibrated solutions. There is abundant evidence for the approximate validity of this assumption for systems involving chromium(III) coordinated to certain monodentate ligands^{3,4} or to 1,3-propanediol. A recent study⁸ shows that rates of displacement reactions of coordination complexes in an ion-exchange resin phase are similar to the rates in aqueous solution. The interpretation to be presented for the 1,2-propanediol-chromium(III)

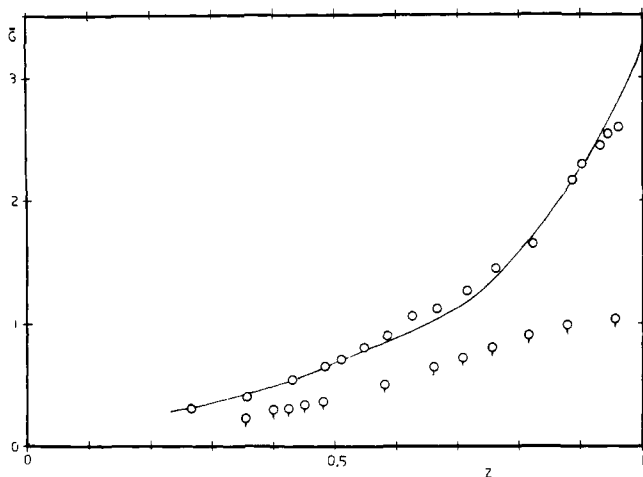


Figure 3. Values of \bar{g} (\bar{g} = (bound glycol)/(total chromium)) as a function of solvent composition (Z = mole fraction of propanediol): O, 1,3-propanediol-chromium(III); ϕ , 1,2-propanediol-chromium(III).

Table I. Values of \bar{g} (\bar{g} = (bound glycol)/(total chromium)) for Chromium(III) Equilibrated in Acidic Aqueous Glycol Mixed Solvents $t = 60^\circ\text{C}$

1,2-Propanediol ([Cr ^{III}] = 0.010 M, [H ⁺] = 0.0989 M)					
Z	\bar{g}^a	recovery ^b	Z	\bar{g}^a	recovery ^b
0.354	0.22	96.1	0.659	0.63	96.7
0.399	0.28	98.5	0.706	0.71	93.9
0.423	0.30	96.8	0.755	0.79	93.2
0.450	0.33	97.5	0.813	0.89	95.6
0.480	0.36	97.3	0.876	0.98	93.9
0.579	0.50	97.9	0.955	1.03	96.0

1,3-Propanediol ([Cr ^{III}] = 0.0096 M, [H ⁺] = 0.129 M)					
Z	\bar{g}^f	recovery ^b	Z	\bar{g}	recovery ^b
0.266	0.30 ^c	98.8	0.713	1.27 ^c	95.7
0.356	0.39	97.1	0.765	1.44 ^c	96.8
0.429	0.54	99.2	0.821	1.64	86.5
0.484	0.65 ^c	99.4	0.886	2.17 ^e	87.4
0.510	0.70	96.0	0.902	2.30	83.1
0.547	0.80	98.1	0.932	2.44	84.8
0.584	0.90	99.4	0.945	2.54 ^c	82.3
0.625	1.06 ^c	96.8	0.963	2.59 ^c	82.4
0.667	1.11 ^d	96.8			

^a Average of duplicate analyses on duplicate sample equilibrated for different times. The average deviation of individual values from the average is 0.014 units of \bar{g} . ^b This is the average of the duplicate samples. ^c Two independent samples studied; duplicate analyses on at least one sample. ^d Three independent samples; duplicate analyses on each sample. ^e Four independent samples; duplicate analysis on one sample. ^f Average of duplicate analysis on single samples unless otherwise noted. The average deviation of the individual values from the average value of \bar{g} is 0.021 units.

system, in contrast, involves the assumption that species containing coordinated 1,2-propanediol are labilized to an extent that would give aquation to monoglycol complexes during the ion-exchange procedure. (It seems likely that this same assumption should be applied to the chromium(III)-ethylene glycol system,² as will be discussed.)

Solutions to be analyzed for values of \bar{g} were equilibrated at 60°C for time periods of 1.5–15 days. (The period was ≥ 10 times the half-time for equilibration for the solvent composition in question.) The chromium(III) ion from a portion of equilibrated solution was quenched with cold ($\sim 0^\circ\text{C}$) dilute (0.10 M) aqueous perchloric acid and treated as already described. Analysis of the eluent for chromium

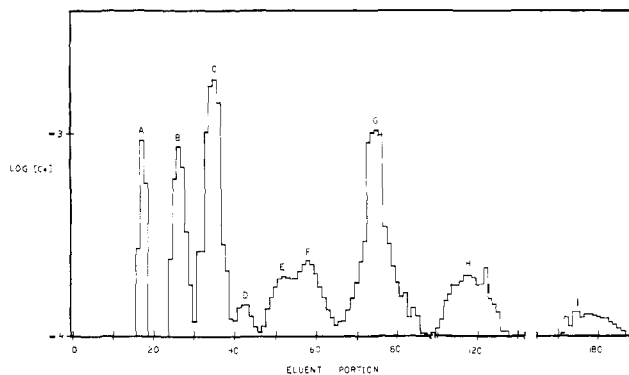


Figure 4. Elution profile for chromium(III)-1,3-propanediol species in solution with $Z = 0.821$ (Equilibration at 60°C). Eluting agent is 3.0 M H_2SO_4 . Peak designations are described in text.

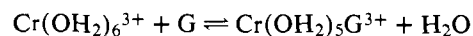
and glycol gave the derived values of \bar{g} presented in Table I and Figure 3.

Separation of Species in Chromium(III)-1,3-Propanediol System. The desirability of separating individual differently solvated chromium(III) ions from the equilibrated aqueous 1,3-propanediol solutions was suggested by the observations for this system (just described) of values of \bar{g} exceeding unity. Such experiments were done for four different compositions of the binary solvent. The elution profile from one of these experiments (at $Z = 0.821$) is presented in Figure 4, and the results are summarized in Table II. In this table, the peaks are designated A through J in order of decreasing ease of elution. (In some elutions, a small amount of chromium(III) is eluted prior to peak A. This eluent, containing in no case more than $\sim 0.3\%$ of the chromium, was not analyzed for glycol, but it was included in calculation of the recovery of chromium(III). This trace of easily eluted chromium(III) species probably is a sulfate complex of charge 1+.) The average values of \bar{g} for the combined portions of eluent comprising each peak are close to integral values in most cases, and these identify the glycol to chromium(III) ratios as A, 0; B and C, 1; D, E, F, and G, 2; and H and I, 3. These data do not, however, establish the number of water molecules coordinated to chromium, and therefore, do not establish how many coordinated glycol molecules are bidentate ligands.

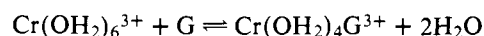
That relatively good separation of different species is achieved in column ion-exchange procedures which extend over periods of many days at $\sim 0^\circ\text{C}$ indicates that interconversion of these species is slow on the time scale of the separation procedure. Minor amounts of interconversion undoubtedly do occur, and this introduces error in the value of \bar{g} in a particular eluent peak. For peak I in the solution with $Z = 0.821$ the identification suggested above is inconsistent with the analyzed value of \bar{g} . Possibly this peak is contaminated with difficultly eluted polymeric species having lower values of \bar{g} . (Calculations to be presented later suggest that the relative amount of chromium in peak I at $Z = 0.821$ is too large.) Such a polymeric species is responsible for peak J in the experiment at $Z = 0.96$.

Derived Results and Discussion

Chromium(III)-1,3-Propanediol Species. Both the values of \bar{g} for chromium(III) in equilibrated solutions and for the species separated from one another in the long column ion-exchange experiments show that species containing at least three coordinated glycol molecules form in this system. These data do not, however, establish the number of coordinated water molecules. This information can be obtained from the dependence of the relative concentrations of various species upon the solvent composition. Chemical equations for formation of the two possible monoglycol species from hexa-aquachromium(III) ion:



and



differ in the number of water molecules produced. Equilibrium quotients for the two reactions are

Table II. Amounts^a and Composition^b of Species in Equilibrated Water-1,3-Propanediol Solution ($t = 60\text{ }^\circ\text{C}$, $[\text{Cr}^{\text{III}}] = 0.0096\text{ mol l}^{-1}$, $[\text{H}^+] = 0.129\text{ mol l}^{-1}$)

Z	Elution peak designation									
	A	B	C	D	E	F	G	H	I	J
0.356	146.5 (0.01)	40.4 (1.00)	28.0 (0.94)	3.4 (1.59)	2.5 (2.21)	3.8 (2.00)	3.7 (2.53)			
0.584	74.5 (0.08)	44.2 (1.06)	56.8 (1.11)	6.5 (1.93)	7.9 (2.10)	9.3 (2.05)	12.6 (1.88)			
0.821	10.8 (0.11)	17.1 (1.20)	39.5 (1.15)	4.7 (1.87)	8.3 (1.93)	10.3 (1.94)	40.3 (2.00)	21.9 (2.61)	18.8 (2.08)	
0.96						11.3 (2.26)	26.2 (2.19)	34.2 (2.88)	59.4 (2.93)	97.8 (1.30)

^a Amounts of chromium(III) in micromoles. ^b Values of \bar{g} for material under peak given in parentheses.

Table III. Equilibrium Quotient Values for Formation of Various Chromium(III)-1,3-Propanediol Species^a from Hexaaquachromium(III) Ion ($t = 60\text{ }^\circ\text{C}$, $[\text{H}^+] = 0.129\text{ M}$)

	Z		
	0.356	0.584	0.821
Q_{15}	0.50	0.42	0.35
Q_{14}	0.22	0.23	0.14 ₃
Q_{24}'	0.076	0.044	0.021
Q_{23}'	0.091	0.049	0.015
Q_{22}'	0.034	0.015	0.0057

^a A primed equilibrium quotient, for instance Q_{24}' , is the sum of the equilibrium quotients for formation of isomeric species of the indicated composition.

$$Q_{15} = \frac{[\text{Cr}(\text{OH}_2)_5\text{G}^{3+}](1-Z)}{[\text{Cr}(\text{OH}_2)_6^{3+}]Z}$$

and

$$Q_{14} = \frac{[\text{Cr}(\text{OH}_2)_4\text{G}^{3+}](1-Z)^2}{[\text{Cr}(\text{OH}_2)_6^{3+}]Z}$$

In the solutions with $Z = 0.356$, 0.584 , and 0.821 , the mole fraction of water ($1 - Z$) varies by a factor of ~ 3.6 , and constancy of an equilibrium quotient calculated on the basis of a particular assignment of composition to a species supports that assignment. With the assignment of elution peak B to pentaquaglycolchromium(III) ion and peak C to tetraquaglycolchromium(III), the values of Q_{15} and Q_{14} derived from data at the three values of Z are given in Table III. The $\sim 30\%$ decrease in the calculated value of each of these equilibrium quotients with increase of glycol content of the solvent is much smaller than the variation in calculated values of each of these equilibrium quotients under the alternate assignment (peak B assumed to be tetraquaglycolchromium(III) ion and peak C is pentaquaglycolchromium(III) ion); if this alternate assignment is made the value of Q_{15} changes by a factor of 2.4 (0.34 at $Z = 0.356$ to 0.81 at $Z = 0.821$), and the value of Q_{14} changes by a factor of 5.2 (0.32 at $Z = 0.356$ to 0.062 at $Z = 0.821$).

There are six possible species containing two symmetric glycol molecules per chromium(III) ion, a pair of geometric isomers for each composition $\text{Cr}(\text{OH}_2)_4\text{G}_2^{3+}$, $\text{Cr}(\text{OH}_2)_3\text{G}_2^{3+}$, and $\text{Cr}(\text{OH}_2)_2\text{G}_2^{3+}$. Only four elution peaks corresponding to the bisglycolchromium(III) species were observed. Relative to the concentration of the most easily eluted species (the species eluted under peak D), the concentrations of species eluted under peaks E, F, and G change in proportion to the mole fraction of water ($1 - Z$) raised to the powers -0.7_1 ,

-0.6_6 , and -1.7 , respectively. Each of these exponents, which gives the difference between the number of water molecules coordinated in the bisglycol species in question compared to the most easily eluted bisglycol species, is expected to be an integer. Although these exponents are not integers, they show clearly that the elutability of bisglycol species decreases as the number of coordinated water molecules decreases, a trend also displayed by the monoglycolchromium(III) species. If these nonintegral values are rounded to the nearest integer, the compositions of the species eluted under the several peaks are judged to be: D, $\text{Cr}(\text{OH}_2)_4\text{G}_2^{3+}$; E, $\text{Cr}(\text{OH}_2)_3\text{G}_2^{3+}$; F, $\text{Cr}(\text{OH}_2)_3\text{G}_2^{3+}$; G, $\text{Cr}(\text{OH}_2)_2\text{G}_2^{3+}$.

Equilibrium quotients for formation of bisglycol species from hexaaquachromium(III) ion have been calculated for each of the solvent compositions with $Z \leq 0.82$. These derived quantities, presented in Table III, show the same qualitative dependence upon solvent composition, a decrease with increasing Z , as shown by Q_{15} and Q_{14} . An approximately linear dependence of the logarithm of the equilibrium quotient upon the mole fraction of glycol is observed, as shown in Figure 5.

If the dependence of the equilibrium quotients upon solvent composition was due solely to nonideality of the solvent mixtures, the slope of the plot of $\log Q_{24}'$ vs. Z would be two times that for the plot of $\log Q_{15}$ vs. Z . The slopes actually differ by a factor of ~ 4 . The same factor should relate the slopes of the plots of $\log Q_{22}'$ and $\log Q_{14}$ vs. Z . The observed factor is ~ 5.6 . It can be concluded, therefore, that the ratios of the activity coefficients of each chromium(III)-glycol species to the activity coefficient of hexaaquachromium(III) ion vary with solvent composition in a manner that is different for different species.

The value of ΔS° (and, therefore, the equilibrium quotient) for each reaction contains a contribution from the ratio of symmetry numbers of the reactant and product species.⁹ For each reaction, the equilibrium quotient Q_{gw} can be expressed

$$Q_{gw} = (\sigma_R \sigma_G / \sigma_P) \kappa_1^a \kappa_2^{g-a}$$

in which κ_1 and κ_2 are the intrinsic (i.e., statistically corrected) equilibrium quotients for forming a complex with one monodentate glycol ligand and one bidentate glycol ligand, respectively, a is the number of monodentate glycol ligands ($a = 2g + w - 6$), and σ_R , σ_G , and σ_P are the symmetry numbers of the reactant complex ($\sigma_R = 24$ for hexaaquachromium(III) ion), 1,3-propanediol ($\sigma_G = 2$), and the product complex, respectively. (A factor 2 is incorporated also into the equation for Q_{gw} if the product species is chiral.¹⁰) (In calculating the symmetry number of a species with a chelated glycol molecule, an idealized planar geometry is assumed for each chelate ring. The

Table IV. Comparison of Experimental Values at $Z = 0.5$ of Q_{gw} (for $g = 1$ and 2) with Values Calculated Using $\kappa_1 = 0.032$ and $\kappa_2 = 0.011$

	Q_{15}	Q_{14}	Q_{24}'	Q_{23}'	Q_{22}'
Obsd ^a	0.45	0.22	0.054	0.059	0.020
Calcd	0.38	0.26	0.061	0.068	0.015

^a Interpolated.

symmetry number for the product water and the contribution of coordinated water to the internal symmetry of the chromium(III) species are not considered in the equations for Q_{gw} . The contribution from this factor can be considered to be a constant incorporated in the values for κ_1 and κ_2 .) The values of the various equilibrium quotients Q_{gw} expressed in this way are: $Q_{15} = 12\kappa_1$, $Q_{14} = 24\kappa_2$, $Q_{24}(\text{cis}) = 48\kappa_1^2$, $Q_{23}(\text{fac}) = 96\kappa_1\kappa_2$, $Q_{22}(\text{cis}) = 96\kappa_2^2$, $Q_{24}(\text{trans}) = 12\kappa_1^2$, $Q_{23}(\text{mer}) = 96\kappa_1\kappa_2$, $Q_{22}(\text{trans}) = 24\kappa_2^2$, $Q_{24}' = 60\kappa_1^2$, $Q_{23}' = 192\kappa_1\kappa_2$, $Q_{22}' = 120\kappa_2^2$, $Q_{33}' = (96 + 64)\kappa_1^3 = 160\kappa_1^3$, $Q_{32}' = (96 + 96 + 384)\kappa_1^2\kappa_2 = 576\kappa_1^2\kappa_2$, $Q_{31}' = (96 + 384)\kappa_1\kappa_2^2 = 480\kappa_1\kappa_2^2$, $Q_{30} = 64\kappa_2^3$, $Q_{42}' = (192 + 48)\kappa_1^4 = 240\kappa_1^4$, $Q_{41}' = (384 + 768)\kappa_1^3\kappa_2 = 1152\kappa_1^3\kappa_2$, $Q_{40}' = (384 + 96)\kappa_1^2\kappa_2^2 = 480\kappa_1^2\kappa_2^2$, $Q_{51} = 192\kappa_1^5$, $Q_{50} = 384\kappa_1^4\kappa_2$, $Q_{60} = 64\kappa_1^6$. For reactions forming species with three or more coordinated glycol molecules, the designation of isomer configuration is not included, but each term in the coefficient of a product of intrinsic equilibrium constants is the statistical factor for formation of a particular isomer.

The coordination of successive molecules of neutral monodentate ligands (methanol,³ ethanol,³ and dimethyl sulfoxide⁴) is governed approximately by the statistical contribution to the successive equilibrium constants, and the present data allow checking this point for the chromium(III)-1,3-propanediol system. Since the several equilibrium constants show a dependence upon solvent composition, the correlation must be made for a particular composition; that chosen was $Z = 0.5$. Values of Q_{15} and Q_{24}' interpolated to $Z = 0.5$ were used to calculate $\kappa_1:\kappa_1 = (Q_{15}Q_{24}'/720)^{1/3}$. Similarly, interpolated values of Q_{14} and Q_{22}' were used to calculate $\kappa_2:\kappa_2 = (Q_{14}Q_{22}'/2880)^{1/3}$. (This calculation gives values of κ_1 and κ_2 as the geometric means of the values derived from the equilibrium quotients for formation of monoglycol and bisglycol species, with the latter values doubly weighted since κ^2 occurs in these equilibrium quotients.) The values so-derived are $\kappa_1 = 0.032$ and $\kappa_2 = 0.011$. A summary of the interpolated values of the five equilibrium quotients and the values calculated using these values of the intrinsic constants is given in Table IV. Although the two adjustable parameters (κ_1 and κ_2) do not generate values for the five equilibrium constants which agree exactly with the experimental values, the agreement is good enough to lend support to the overall picture.

Additional correlations are possible. In particular the value of \bar{g} can be calculated for solutions in which there are appreciable concentrations of species containing more than two coordinated glycol molecules. In these calculations the values of κ_1 and κ_2 used to estimate values of Q_{gw} ($g > 2$) for a particular solvent composition were derived from the values of $Q_{24}'(\kappa_1 = (Q_{24}'/60)^{1/2})$ and $Q_{22}'(\kappa_2 = (Q_{22}'/120)^{1/2})$ for that same solvent composition as given by the plots in Figure 5. The values of \bar{g} calculated in this way for all solvent compositions studied at $Z \leq 0.902$ agree with the experimentally determined values (Table I) with an average deviation of 0.04 units of \bar{g} . (The solid line in Figure 3 is based upon these calculated values of \bar{g} .)

Elution peaks H and I, containing species with three coordinated molecules of 1,3-propanediol, are observed in solutions

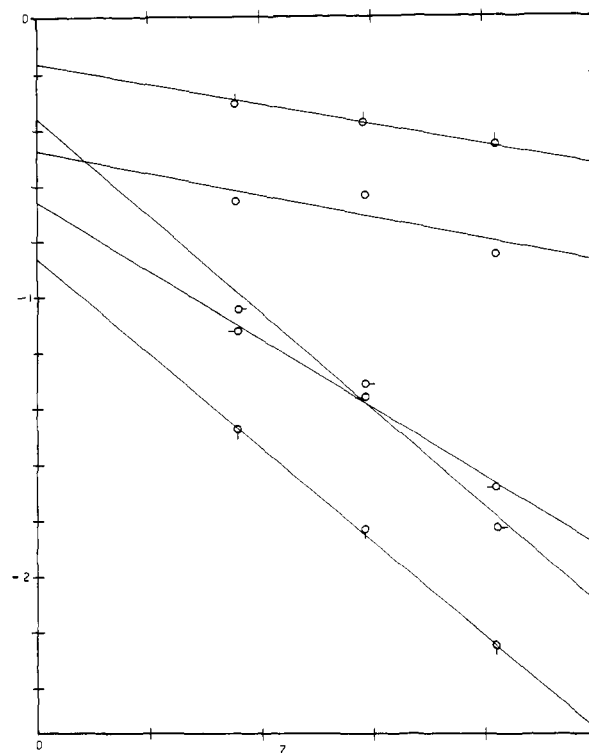


Figure 5. The dependence of Q_{gw} upon solvent composition. Reading down at $Z = 1$: Q_{15} , \circ ; Q_{14} , \circ ; Q_{24}' , \circ ; Q_{23}' , \circ ; Q_{22}' , \circ . Each line correlating Q_{gw} with Z has the form $\log Q_{gw} = \alpha + \beta Z$. The values of α and β are: Q_{15} , 0.182, 0.336; Q_{14} , 0.47, 0.40; Q_{24}' , 0.66, 1.22; Q_{23}' , 0.36, 1.74; Q_{22}' , 0.86, 1.68.

with $Z = 0.821$ and 0.96. The change in relative amounts of chromium in these two peaks with change of Z shows that peak I contains a species with fewer water molecules than contained in the species eluted as peak H. For $Z = 0.821$, the value of Q_{31} calculated from the amount of chromium in peak H is 1.5 times the value calculated using the values of κ_1 and κ_2 determined from values of Q_{24}' and Q_{22}' observed for this solvent. This agreement is better than corresponds to any other assignment of composition to the species. The peaks H and I are, therefore, assigned: H, $\text{Cr}(\text{OH})_2\text{G}_3^{3+}$; I, CrG_3^{3+} . (The amount of chromium present in peak I in the solution with $Z = 0.821$ is fivefold larger than calculated using the value of κ_2 , supporting the suggestion that this peak is contaminated with other species. The observed relative amounts of chromium(III) in elution peaks H and I in the solution with $Z = 0.96$ is ~ 1.5 -fold larger than expected on the basis of values of κ_1 and κ_2 and the value of $(1 - Z)$, a relatively uncertain quantity.)

Other triglycol species are possible, but species containing relatively more coordinated water molecules are unimportant for solutions of high Z (low $(1 - Z)$). With values of κ_1 and κ_2 extrapolated to $Z = 1$, it can be calculated that the maximum expected value of \bar{g} is 3.27.

Chromium(III)-1,2-Propanediol Species. The particularly striking behavior observed for the ethylene glycol-chromium(III) system,² mentioned in the introduction, is observed also for the 1,2-propanediol-chromium(III) system. The relatively rapid spectral change which occurs upon dilution with aqueous acid of a previously equilibrated solution is a key observation, but first the limiting value of $\bar{g} \approx 1$ will be considered. If it were simply a lower stability of the 1,2-propanediol-chromium(III) species compared to the 1,3-propanediol-chromium(III) species that causes \bar{g} not to exceed 1.0 appreciably,¹² the slope of the plot \bar{g} vs. Z would not be getting smaller at high Z , as is observed. This point also can be checked in quantitative calculations.

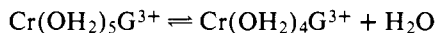
Because of the presence of both chelated and nonchelated species and the dependence of Q values upon Z , the form of the function $\bar{g}(Z)$ is very complicated. The two systems can be compared roughly, however, by considering the values of the quantity $(\bar{g}/(6 - \bar{g}))$. Values of the quotient $(\bar{g}/(6 - \bar{g}))_{1,2}/(\bar{g}/(6 - \bar{g}))_{1,3}$ might be expected to be approximately constant as Z is varied if lower stability of the 1,2 system were the explanation for the observations. This ratio decreases by a factor of 2 in going from $Z = 0.35$ to $Z = 0.95$.

Since species containing only monodentate glycol are among the species observed for the 1,3-propanediol-chromium(III) system, the formation of only such species, $\text{Cr}(\text{OH})_2\text{G}_g^{3+}$, might reasonably be postulated for the 1,2 system if it were assumed that strain prevented formation of chelated 1,2-propanediol-chromium(III) species. If these species with nonchelated glycol, $\text{Cr}(\text{OH})_2\text{G}_g^{3+}$, were formed with the relative stabilities of the several species being determined only by the statistical factor, the statistically corrected equilibrium quotient κ_1 would be related to $\bar{g}(Z)$:

$$\kappa_1 = \bar{g}(1 - Z)/(6 - \bar{g})Z$$

Values of κ_1 calculated from the data in Table I are relatively constant for the solutions with $Z \leq 0.480$ ($\kappa_1 = 0.0710 \pm 0.0014$), but they decrease steadily for $Z \geq 0.579$, becoming $\kappa_1 = 0.0276$ at $Z = 0.876$, and $\kappa_1 = 0.0098$ at $Z = 0.955$. If $\kappa_1 = 0.071$ governed the coordination of 1,2-propanediol to chromium(III), the value of \bar{g} would exceed 1.0 at $Z \geq 0.74$ and would be 2.0 and 3.6 at the highest values of Z studied. The failure to observe $\bar{g} > 1$ at high values of Z is not, therefore, consistent with the $\bar{g}(Z)$ data at low values of Z .¹³ This argument is marred, of course, by the probable existence of medium effects similar to those observed for the 1,3-propanediol-chromium system. Although the data are not absolutely conclusive, it seems reasonable to explain the failure to detect 1,2-propanediol-chromium(III) and ethylene glycol-chromium(III)² species with $\bar{g} > 1$ as being due, not to their thermodynamic instability, but rather to lability which does not allow them to survive the ion-exchange procedure.

Observations in both the earlier study of ethylene glycol-chromium(III) species and the present study of 1,2-propanediol-chromium(III) species indicate that a relatively rapid change occurs when the solvent composition of a solution containing monoglycolchromium(III) ion is altered. The linear dependence of k' upon $(1 - Z)$ (Figure 2) is consistent with the reaction



in which the nonchelated and chelated monoglycol species are transformed into one another. The rapid occurrence of this reaction also would explain the failure to detect species with $g > 1$ by the ion-exchange procedure if a chelated 1,2-glycol causes labilization of ligands bonded at all other coordination sites. In this model for the behavior of 1,2-glycol-chromium(III) species, labilization occurs only when one (or more) glycol molecules is chelated, but the relatively rapid interconversion of nonchelated and chelated species provides a pathway for aquation of $\text{Cr}(\text{OH})_2\text{G}_2^{3+}$ during the ion-exchange separation.

If, during the ion-exchange procedure, all species containing two or more coordinated glycol molecules aquate to species containing one glycol molecule, the equation relating \bar{g} to solvent composition is

$$\bar{g} = \frac{\sum Q_{gw} Z^g / (1 - Z)^{6-w}}{1 + \sum Q_{gw} Z^g / (1 - Z)^{6-w}}$$

(This equation is the same as that which follows directly from the definition of \bar{g} except that a coefficient g in each term in the numerator is replaced by a coefficient of unity.) There is

Table V. Comparison of Stabilities of Chromium(III)-Glycol Species

Z	\bar{g}		
	Ethylene glycol ^a	1,2-Propanediol ^b	1,3-Propanediol ^b
0.27	0.18		0.30
0.35	0.24	0.22	0.39

^a Reference 2 (60 °C). ^b This work (60 °C).

no reason, however, to expect the equilibrium quotients for the chromium(III)-1,2-propanediol system to be medium-independent since those for the chromium(III)-1,3-propanediol system vary appreciably with solvent composition. Under these circumstances no uniqueness can be claimed for the values of Q_{gw} obtained from fitting of the apparent values of \bar{g} to a function of Z . It seems likely, therefore, that the values of Q_{15} and Q_{14} reported earlier² for the chromium(III)-ethylene glycol system (called Q_1 and (Q_1Q_{11})) are not reliable measures of the stability of such species.

The activation parameters for the slow equilibration ($\Delta H^\ddagger(k) = 25.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger(k) = 2.4 \text{ cal mol}^{-1} \text{ K}^{-1}$) and the relatively rapid reequilibration upon dilution ($\Delta H^\ddagger(k') = 14.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger(k') = -20.9 \text{ cal mol}^{-1} \text{ K}^{-1}$) observed for the chromium(III)-1,2-propanediol system are very close to the values observed for the chromium(III)-ethylene glycol system² (24.6 kcal mol⁻¹ and 1.1 cal mol⁻¹ K⁻¹ for k_1 and 14.7 kcal mol⁻¹ and -23.1 cal mol⁻¹ K⁻¹ for k_2).¹¹ The interpretation of the relatively rapid spectral change as being due to chelate ring closure is supported by the negative value of ΔS^\ddagger for this process.

Comparisons with Other Systems. In the absence of reliable values of equilibrium quotients for chromium(III)-1,2-glycol systems, comparison of stabilities of the glycol systems which have been studied can be made simply on the basis of values of \bar{g} observed in solvents of low Z . Such a comparison is given in Table V.

The stabilities of chromium(III)-1,2-glycol species are very similar for the two systems, and this similarity extends to higher values of Z . This allows a tentative conclusion that coordination of chromium(III) to primary and secondary alcohol groups has similar stability. The chromium-1,3-propanediol species are appreciably more stable than species involving 1,2-glycols, but it is not possible to evaluate the extent to which this is due to greater stability of chelate species of 1,3-propanediol. At these values of Z , less than one-half of chromium(III)-1,3-propanediol species involve chelated glycol, and the relative amount of chelated species may be lower for the chromium(III)-1,2-diol systems.

It is possible, however, to compare the value of κ_1 obtained for chromium(III)-1,3-propanediol species with the corresponding statistically corrected equilibrium quotients for coordination of methanol and ethanol to chromium(III). The values for 60 °C (based upon values of equilibrium quotients extrapolated to $Z = 0$) are: methanol, $\kappa_1 = Q_1/6 = 0.11$; ethanol, $\kappa_1 = Q_1/6 = 0.07$; and 1,3-propanediol, $\kappa_1 = Q_{15}/12 = 0.055$. If, however, the equilibrium constants are written for reactions involving the ligand in the gas phase, the comparison becomes: methanol, $\kappa_1 = 1.9 \times 10^{-4} \text{ Torr}^{-1}$; ethanol, $\kappa_1 = 2.3 \times 10^{-4} \text{ Torr}^{-1}$; and 1,3-propanediol, $\kappa_1 = 5.3 \times 10^{-2} \text{ Torr}^{-1}$. As suggested earlier,² the greater stability of the nonchelated metal-diol complex, relative to the complexes involving simple alcohols, is probably due to hydrogen bonding interactions between the solvent and the free hydroxyl groups of the coordinated ligands. This outer-sphere solvation also diminishes the chelate-effect in the chromium(III)-1,3-propanediol

system. One measure of this effect is the equilibrium quotient for the reaction in which the monodentate complex, $\text{Cr}(\text{OH}_2)_5\text{G}^{3+}$, is converted to the bidentate complex, $\text{Cr}(\text{OH}_2)_4\text{G}^{3+}$; the statistically corrected value of this equilibrium quotient is κ_2/κ_1 , which, for $Z = 0.5$, is $(0.011/0.032) = 0.34$.

References and Notes

- (1) Based in part upon the Ph.D. Thesis of K. C. Showalter, University of Colorado, 1975.
- (2) H. B. Klonis and E. L. King, *Inorg. Chem.*, **11**, 2933 (1972).
- (3) C. C. Mills, III, and E. L. King, *J. Am. Chem. Soc.*, **92**, 3017 (1970).
- (4) L. P. Scott, T. J. Weeks, Jr., D. E. Bracken, and E. L. King, *J. Am. Chem. Soc.*, **91**, 5219 (1969).
- (5) G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 414 (1952).
- (6) R. Sargent and W. Rieman, III, *Anal. Chim. Acta*, **14**, 381 (1956).
- (7) E. A. Guggenheim, *Philos. Mag.*, **2**, 538 (1926).
- (8) I. B. Liss and R. K. Murmann, *Inorg. Chem.*, **14**, 2314 (1975).
- (9) S. W. Bensen, *J. Am. Chem. Soc.*, **80**, 5151 (1958).
- (10) V. Gold, *Trans. Faraday Soc.*, **60**, 738 (1964).
- (11) These values for the ethylene glycol system are values associated with rate constants k_1 and k_2 (in the notation of the earlier paper) for the conversion of $\text{Cr}(\text{OH}_2)_6^{3+}$ to $\text{Cr}(\text{OH}_2)_5\text{G}^{3+}$ and the conversion of $\text{Cr}(\text{OH}_2)_5\text{G}^{3+}$ to $\text{Cr}(\text{OH}_2)_4\text{G}^{3+}$, respectively. The values for the 1,2-propanediol system are for the composite sum of rate constants which determine the rate of equilibration.
- (12) In the present study the value of \bar{g} exceeds one (1.03) at $Z = 0.955$, and in the study of ethylene glycol-chromium(III) (ref 2), values of \bar{g} at $Z = 0.980$ and 0.988 exceeded one (1.02 and 1.04, respectively). It is possible that inadequate rinsing of the ion-exchange resin prior to elution is responsible for these values of \bar{g} greater than one.
- (13) In the study of the ethylene glycol-chromium(III) system (ref 2), separation by ion-exchange of different glycol-chromium(III) species was attempted for equilibrated solutions with $Z = 0.335, 0.539, 0.730, 0.950$, and 0.980. In each case, only two electron peaks were observed. The more easily eluted species was hexaaquachromium(III) ion, and the less easily eluted species had a value of $\bar{g} = 1.00 \pm 0.02$.

Energy Transfer from the Second Triplet State of Naphthalene and Other Aromatic Compounds¹

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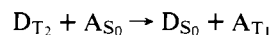
Abstract: Energy transfer from the second triplet state of naphthalene, 1-chloronaphthalene, and pyrene was examined with the naphthalene systems studied in more detail. A modified chemical method was designed in order to increase trapping efficiency of the very short lived upper states. The method involved the use of a third compound at high concentration which trapped the T_2 of the donor and carried excitation to the eventual acceptor via excitation hopping through identical molecules. Chemistry produced by the triplet acceptor provided the handle to follow the energy transfer processes. In the case of naphthalene the energy carrier was benzene and the best acceptor was *endo*-dicyclopentadiene. The average lifetimes of the T_2 state of naphthalene and 1-chloronaphthalene were found to be 12 ± 2 , 13 ± 2 ps, respectively. These values are an order of magnitude smaller than the corresponding values for substituted anthracenes (200–300 ps). From the difference in T_1 – T_2 separation of the two compounds, this difference in lifetime was not unexpected.

Introduction

The presence of a second triplet state below the lowest excited singlet in aromatic compounds was first suggested by the triplet yield data. The generally high values are inconsistent with the sizable S_1 – T_1 splitting in these compounds if assuming intersystem crossing involves these two states only.² This suspicion was subsequently confirmed by several groups through detection of low-lying second triplet levels in these molecules. Therefore, by flash-photolysis studies Kellogg³ and McCartin and Bennett⁴ placed the T_2 state of anthracene and several substituted anthracenes below the corresponding S_1 . Similarly picene and pyrene were shown to have low-lying T_2 states (in the latter case T_2 is slightly above S_1).⁵ By direct singlet-triplet absorption measurements a low-lying T_2 state was also detected in benzene⁶ and naphthalene.⁷ The T_1 – T_2 separations in the latter two cases are too small for convenient triplet-triplet absorption studies. The high triplet yields in these compounds are therefore a result of rapid intersystem crossing between the nearly isoenergetic S_1 , T_2 states, followed by internal conversion between the triplet states.

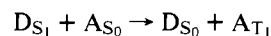
A small S_1 – T_2 separation implies an unusually large T_1 – T_2 gap. This was verified in the above mentioned spectroscopic studies. One may then logically consider the possibility that such a molecule may pause at an excited triplet level for a rather long period before undergoing internal conversion to T_1 . Indeed, soon after Kellogg's assignment of the T_2 level of anthracene, Liu and Edman⁸ presented evidence that such

states can participate in biomolecular processes. Many of the substituted anthracene-sensitized reactions were shown to involve triplet-triplet energy transfer from the second triplet states:⁹



Kinetic studies of these systems provided then the only available method to determine the average lifetime of such excited triplets. Subsequently spectroscopic studies of the anthracene-sensitized naphthalene phosphorescence in mixed crystals¹⁰ and chrysene-sensitized (two-photon excitation) phosphorescence of biphenyl in toluene matrix¹¹ established the case of energy transfer from T_2 beyond reasonable doubt.

Nevertheless, a paper¹² did appear to suggest the above mentioned results could be instead due to the following spin-forbidden process:



The observation of fluorescence quenching enhanced by heavy atoms was considered as supporting evidence for this process. However, the observation that singlet quenching is not accompanied by formation of the acceptor triplets as shown in an experiment of 9,10-dibromoanthracene-sensitized photodimerization of 1,3-cyclohexadiene¹³ negates such a possibility. The spin-forbidden process, however, does appear to take place in other selected systems at expectedly a much slower rate.¹⁴