

Figure 1.

dron about the rhenium, the chief deviations being in the angles of only $\sim 79^\circ$ made by the Re-Cl (out of plane) bonds with the Re_3 plane. This is readily attributable to van der Waals repulsions. The Re-Cl (in plane) distances are decidedly long (2.52), while the other two types of Re-Cl bonds are of about normal length for single bonds.

The very short Re-Re distances are of great interest. They indicate that, while the bridging chlorine atoms may play a role in holding the triangular array of rhenium atoms together, there is strong metal-metal bonding.³ It appears that a satisfactory first-order treatment of the metal-metal bonding can be given using an LCAO-MO approach. Each rhenium atom is taken to form a set of hybrid, octahedrally directed σ orbitals, of which five are used to bind chlorine atoms and the sixth points to the center of the triangle. These then combine to form a bonding (A') and an antibonding (E') MO. Similarly, the d_{xy} , d_{xz} and d_{yz} orbitals of each rhenium atom combine to give bonding and antibonding, 3-center MO's. There are just six bonding orbitals which are filled by the twelve electrons, thus accounting for the experimentally observed diamagnetism. The structure and bonding in $[\text{Re}_3\text{Cl}_{12}]^{3-}$ have been found to exhibit certain striking similarities to what is found in the $[\text{Mo}_6\text{X}_8]^{4+}$ and $[\text{M}_6\text{X}_{12}]^{2+}$ systems⁸; these relationships will be discussed separately.⁸

The structure of the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ ion leads to the consideration of some related plausible structures for some other Re^{III} complexes. For example, the compounds⁹⁻¹¹ ReLCl_3 ($L = \text{py}$, $(\text{C}_6\text{H}_5)_3\text{P}$ or $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2\text{P}$) seem likely to have similar trimeric structures in which the three in-plane Cl^- ions are replaced by the neutral ligands L . ReCl_3 has long been known¹² to give

(3) In rhenium metal, the Re-Re distances are 2.74 and 2.76 Å.⁴ In the polynuclear cations, $[\text{Mo}_6\text{Cl}_8]^{4+}$, $[\text{Nb}_6\text{Cl}_8]^{2+}$, $[\text{Ta}_6\text{Cl}_8]^{2+}$ and $[\text{Ta}_6\text{Br}_8]^{2+}$, which contain octahedra of metal atoms,⁵ the metal-metal distances are, respectively, 2.63, 2.85, 2.90 and 2.90 Å. In $\text{Os}_3(\text{CO})_{12}$ the Os-Os distances⁶ are 2.88 ± 0.01 Å. Comparison with these data would indicate that the Re-Re bonding in $[\text{Re}_3\text{Cl}_{12}]^{3-}$ must be quite strong. Pauling⁷ predicts a distance of ~ 2.56 Å. for a Re-Re single bond.

(4) C. T. Sims, C. M. Craighead and R. I. Jaffee, *J. Metals*, **7**, 168 (1955).

(5) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 440.

(6) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(7) Reference 5, p. 403.

(8) T. E. Haas and F. A. Cotton, to be published.

(9) M. Freni and V. Valenti, *Proc. Intern. Cong. Pure Appl. Chem.*, 17th, Munich, 1959, Abstract A1057.

(10) R. Colton, R. Levitus and G. Wilkinson, *J. Chem. Soc.*, 4121 (1962).

(11) J. Chatt and G. A. Rowe, *ibid.*, 4019 (1962).

(12) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford, 1950, p. 1313. There is a report that the material is polymeric in solution, though it is claimed that it is a dimer rather than a trimer as we

aqueous solutions which, when freshly prepared, contain insufficient free Cl^- ion to afford a precipitate with Ag^+ . Such solutions might contain $\text{Re}_3\text{Cl}_9(\text{H}_2\text{O})_3$ species in which the in-plane Cl^- ions of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ have been replaced by H_2O . One final example of the possible significant implications of the structure reported here, this relating to a compound of a different heavy metal, is the possibility that the reported compound¹³ $\text{K}_3\text{W}_3\text{Cl}_{14}$ is in fact $\text{K}_3\text{W}_3\text{Cl}_{12}$, containing a $[\text{W}_3\text{Cl}_{12}]^{6-}$ ion, isoelectronic and isostructural with the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ ion (W^{II} and Re^{III} are isoelectronic). These and various other possible inferences from the $\text{Cs}_3[\text{Re}_3\text{Cl}_{12}]$ structure are under active investigation in this Laboratory.

Acknowledgment.—The generous support of this work by the National Science Foundation is gratefully acknowledged.

might suppose. Any partial decomposition or impurities would tend to give a low molecular weight as obtained by measurements of colligative properties.

(13) R. A. Laudise and R. C. Young, *J. Am. Chem. Soc.*, **77**, 5288 (1955). The authenticity of the formula previously given is dubious, because the levels of the impurities, $\text{K}_3\text{W}_2\text{Cl}_9$ and KCl , were so great that they were evident even in powder X-ray photographs.

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THE IMPORTANCE OF GROUND STATE SOLVATION IN THE SOLVOLYSIS OF *t*-BUTYL CHLORIDE^{1,2}

Sir:

We wish to report direct calorimetric measurements of the partial molal heats of solution ($\Delta\bar{H}_s$) for *t*-butyl chloride and several other compounds in a series of aqueous ethanol solutions. A number of authors³⁻⁶ have observed sharp minima in ΔH^* for $\text{S}_{\text{N}}1$ solvolyses of several substrates in aqueous binary solvents between 0.6 and 0.95 mole fraction water. Our results show clearly that for the solvolysis of *t*-butyl chloride in aqueous ethanol at least 95% of the variation of ΔH^* in the region of the minimum³ can be accounted for by changes in ground state solvation leaving transition state changes negligible.

Activation parameters for reactions in solution are defined as the differences in free energy, enthalpy or entropy between the solvated ground state and solvated transition state. There is no way of deciding how much of the variation of ΔH^* or ΔS^* should be ascribed to changing solvation of either state until standard enthalpies and entropies of solution for ground states are measured in each solution for which activation parameters are known; the sum of the two then by definition will give the thermodynamic properties for the transition state.^{3,7,8} It usually is suggested that the needed data for $\Delta\bar{H}_s$ and $\Delta\bar{S}_s$ should be obtained from the temperature coefficient of the Henry's law constant ($\Delta\bar{F}_s^0$). As compared with direct calorimetric measurement this requires a prohibitive amount of labor, is inherently less accurate and may be experimentally impractical in cases (such as that discussed

(1) Solvent Effects in Organic Chemistry I.

(2) This work was supported by National Science Foundation Grant G-14583. We are most appreciative of this assistance.

(3) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

(4) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 931 (1956).

(5) J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 5129 (1960); **84**, 2914 (1962).

(6) E. Tommila, *et al.*, *Acta Chem. Scand.*, **9**, 975 (1955); **6**, 844 (1952); **9**, 989 (1955); *Ann. Acad. Sci. Fennicae, Ser. A*, **II**, No. 65 (1955), and other papers.

(7) R. A. Clement, J. N. Naghizadeh and M. R. Rice, *J. Am. Chem. Soc.*, **82**, 2449 (1960).

(8) R. E. Robertson, R. L. Heppollette and J. M. W. Scott, *Can. J. Chem.*, **37**, 803 (1959).

TABLE I^a

Mole fraction water	$\Delta\bar{H}_s$, kcal./mole	$\Delta\Delta\bar{H}_s$, kcal./mole	<i>t</i> -Butyl chloride ΔH^* , ^b kcal./mole	$\Delta\Delta H^*$, ^b kcal./mole	$\frac{\Delta\Delta H^*}{\Delta\Delta\bar{H}_s}$	<i>t</i> -Butanol $\Delta\bar{H}_s$, kcal./mole	Carbon tetrachloride $\Delta\bar{H}_s$, kcal./mole	Experimental error in $\Delta\bar{H}_s$, kcal./mole
0.929 ± 0.005	2.35	0.0	22.01 ± 0.15	0.0		-2.56	0.0	±0.16
0.906	3.05	0.70	21.20	-0.81	-1.16	-1.76	0.64	.16
.884	3.68	1.33	20.57	-1.44	-1.08	-0.70	2.15	.16
.857	4.20	1.85	20.20	-1.81	-0.98	-0.39	2.55	.15
.830	3.97	1.62	20.32	-1.69	-1.04	0.0	3.05	.15
.798	3.30	0.95	21.05	-0.96	-1.01	.0	3.10	.14
.765	2.80	0.45	21.63	-0.38	-0.84	.28	2.65	.14
.726	2.60	0.25				.40	2.25	.14
.684	2.20	-0.15	21.67	-0.34	2.27	.26	1.57	.13
.582	1.80	-0.55	21.90	-0.11	5.00	.0	1.20	.12

^a All properties measured at 25°. All $\Delta\bar{H}_s$ values are referred to a standard state of pure liquid solute at 25° so that $\Delta\bar{H}_s = \bar{H}$ (solute in solution) - \bar{H} (pure solute). ^b See ref. 3.

here) where the substrate undergoes rapid solvolysis.

Our work was done with a specially designed rapid response (5-10 sec.) recording calorimeter (to be described in detail subsequently) in which error from the heat of solvolysis could be eliminated. By means of a thermistor and bridge circuit going to a 1-mv. recorder, temperature changes of $\pm 0.0003^\circ$ were detectable so that when 3×10^{-4} mole samples of solute were introduced into 115 ml. of solvent in a doubly insulated calorimeter, partial molal enthalpy changes could be obtained directly, as shown by independent experiments. The heat capacity of the calorimeter and its contents was measured by using heat from a standard resistor before and after each addition of solute. This also served to calibrate the entire apparatus in terms of measured calories. Each measurement of $\Delta\bar{H}_s$ in Table I represents the average of at least three completely independent experiments. Our equipment can be used with accuracy and precision that compare well with the best ΔH^* data (± 150 cal./mole) for *t*-butyl chloride solvolysis.³ Evidence of its reliability is given by close agreement with the results of Giauque, Hornung, Kunzler and Rubin⁹ for the partial molal heat of dilution of sulfuric acid with water. For 39.94% sulfuric acid they get -0.348 kcal./mole while our value is -0.336 ± 0.12 kcal./mole, and for 80.53% sulfuric acid they get -3.574 kcal./mole while we measure -3.591 ± 0.045 kcal./mole. As shown in Table I our error for the results described there is somewhat higher because insolubility of these solutes forced us to use smaller than optimum samples. This difficulty also prevented us from making accurate measurements on *t*-butyl ethyl ether which otherwise would be included in the table. An additional check that our measurements are of the same order of magnitude as those obtained from Henry's law temperature coefficients is shown by the fact that Winstein and Fainberg³ calculate a $\Delta\Delta\bar{H}_s$ of 3.0 kcal./mole for the change in heat of solution for *t*-butyl chloride going from methanol to 70% aqueous methanol while our value is 2.0 kcal./mole, which is probably more accurate by virtue of the method used.

Our actual values will differ by the heat of vaporization from the $\Delta\bar{H}_s$ obtained through the temperature coefficient of Henry's law. However, it is $\Delta\Delta\bar{H}_s$ that is important for the argument and that will be independent of the method.

The results presented in Table I and Fig. 1 show that the enthalpies of solution for *t*-butyl chloride, carbon tetrachloride and *t*-butyl alcohol all pass through endothermic maxima in the same region of solvent composition where the ΔH^* minimum occurs. It should be noted that within experimental error, $\Delta\Delta\bar{H}_s$ for the

ground state of *t*-butyl chloride is equal and opposite in magnitude to $\Delta\Delta H^*$ in the region where this parameter has its minimum. Apparently, as the solvent becomes less aqueous this direct relation breaks down. Similar measurements on cyclohexane show no measurable change in $\Delta\bar{H}_s$ through this solvent range although because of low solubility and small values of $\Delta\bar{H}_s$ the results for that compound are of lower reliability than those tabulated.

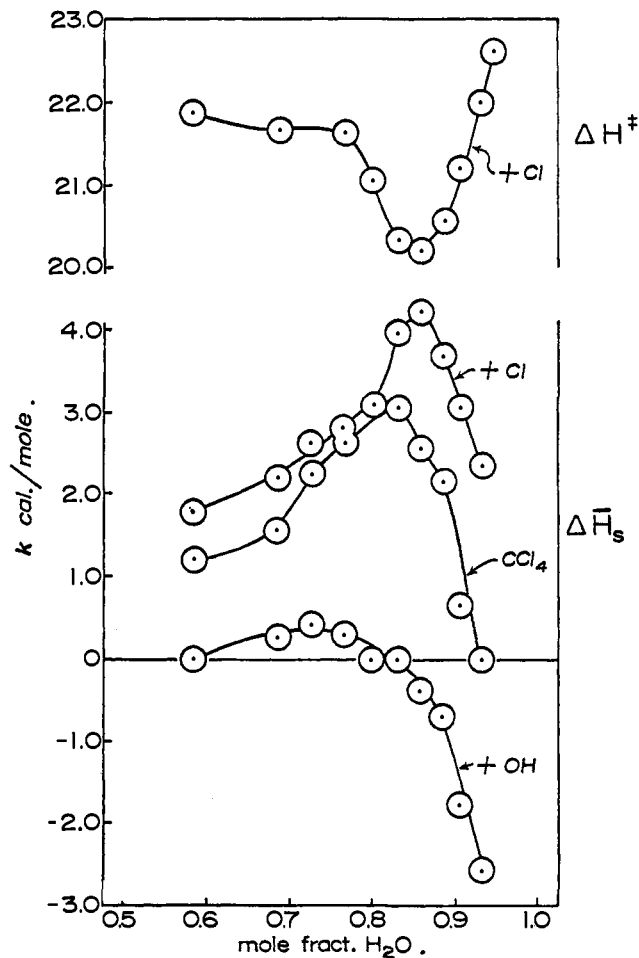


Fig. 1.—Variation of enthalpy of activation³ for solvolysis of *t*-butyl chloride and enthalpy of solution of *t*-butyl chloride, carbon tetrachloride and *t*-butyl alcohol in aqueous ethanol solutions.

Careful examination of what values are available for $\Delta\bar{H}_s$ of salts in aqueous alcohols^{10,11} suggests that the failure of the *t*-butyl chloride transition state to exhibit

(9) W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

(10) R. L. Moss and J. H. Wolfenden, *J. Chem. Soc.*, 118 (1939).

(11) C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2430 (1940).

a minimum heat of solution in this region of the solvent spectrum might have been expected if its solvation behavior were similar to that of tetramethylammonium chloride.³

It is tempting to theorize about the reason for the sudden solvation changes that occur in these solvent mixtures. However, further measurements that we are currently making on other solute-mixed solvent systems suggest that it will be prudent to defer speculation until more data are available.

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POLYNUCLEOTIDES. V. HELIX-COIL TRANSITION OF POLYRIBOGUANYLIC ACID^{1,2}

Sir:

We wish to present evidence that polyriboguanylic acid³ (poly G), like other homopolynucleotides,⁴ can exist in two distinct macromolecular conformations. One of these is apparently a single-stranded form, devoid of secondary structure, that occurs either in neutral solution of low ionic strength at temperatures close to 100° or in strongly alkaline solution. Under a

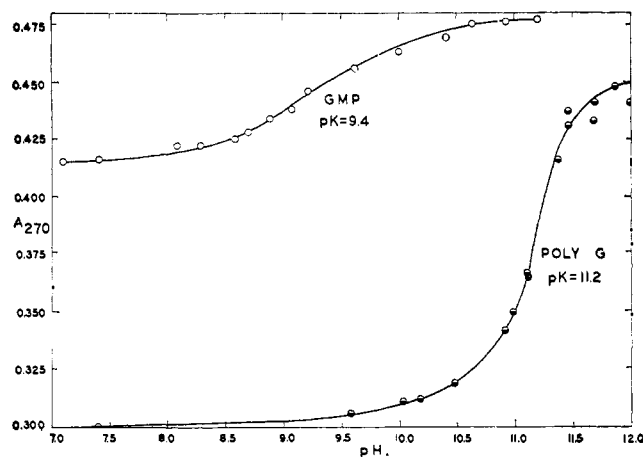


Fig. 1.—Spectrophotometric titration of poly G and its alkaline hydrolysis products (2'-GMP + 3'-GMP) at the same concentration, $4.3 \times 10^{-6} M$, in $0.2 M Na^+$ at 25° .

wide range of solvent conditions removed from these extremes of temperature or pH, poly G exists as a multi-stranded helix. The two forms of poly G are interconvertible, and have been distinguished in very dilute polymer solution on the basis of several physical properties that are sensitive to secondary structure in polynucleotides.

Alkaline Transition.—On titration with alkali, the monomer, guanosine monophosphate (GMP) displays

(1) The last paper in this series was by J. R. Fresco and D.-F. Su, *J. Biol. Chem.*, **237**, PC 3305 (1962).

(2) This investigation was supported by grants from the United States Public Health Service, the National Science Foundation, and the American Heart Association.

(3) Poly G, synthesized enzymatically,¹ was purified by phenol extraction and extensive dialysis to remove proteins, divalent cations and very short oligonucleotides.

(4) Polyadenylic acid: J. R. Fresco and P. Doty, *J. Am. Chem. Soc.*, **79**, 3928 (1957); polyuridylic acid: M. Lipsett, *Proc. Natl. Acad. Sci.*, **46**, 445 (1960); polycytidylic acid: J. R. Fresco, R. Brown and P. Doty, in preparation; polyinosinic acid: A. Rich, *Biochim. Biophys. Acta*, **29**, 502 (1958).

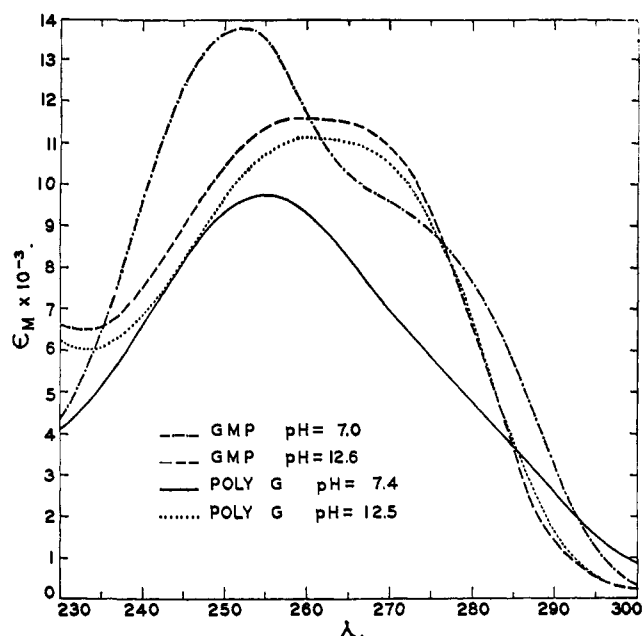


Fig. 2.—Near-ultraviolet absorption spectra of poly G and GMP in $0.6 M Na^+$ at 25° .

an isobestic point at $260.5 m\mu$. The $-HN-CO-$ group being titrated in this region has a pK of 9.4 (Fig. 1). By contrast, when poly G is so titrated in $0.2 M Na^+$ at 25° , the pK is shifted to 11.2 (Fig. 1) and there is a significant hyperchromic change at $260.5 m\mu$ (see Fig. 2). In addition, the complete titration of the polymer occurs within one pH unit. It can also be seen from Fig. 2 that poly G is markedly hypochromic, relative to GMP, at neutral pH, but only slightly so at high pH. Complete alkaline titration of poly G brings about other changes as well. There is a dramatic decrease in specific rotation (from 100° to -38° at $589 m\mu$) that does not occur with the monomer ($[\alpha]_D$ for 2'-GMP changes only from -26° to -32°), as well as a marked change in the rotatory dispersion. The sedimentation constant (in $0.2 M Na^+$ to minimize charge repulsion effects) also changes, reversibly, by more than a factor of 2 (in one case from $3.6 s_{w,20}$ to $1.6 s_{w,20}$ and back to $3.4 s_{w,20}$ on reneutralization).

These observations are most simply interpreted in terms of an alkali-induced, cooperative, helix-coil transition. We deduce that the helix is multistranded, has a right-handed sense of twist,⁵ and contains stacked sets of hydrogen-bonded guanine residues.

Thermal Transition.—Denaturation of the helix can also be achieved thermally. At pH 7 the helix is exceptionally stable, and the transition, as indicated by the hyperchromic change, is not complete at 100° , even in a solvent of very low ionic strength ($0.002 M Na^+$). As the pH is raised, the transition occurs at lower temperatures. Increasing the ionic strength stabilizes the helical structure, and can counteract, in part, the effect of elevated pH. The addition of 1-butanol to the aqueous neutral solvent weakens the helix. The breadth of these helix-coil transitions is somewhat greater than usual for polynucleotide helices, and varies with the preparation of poly G. This is probably because of the very considerable molecular weight polydispersity among the single strands of poly G (observed in the ultracentrifuge) that interact to form helices and may also be due to imperfections in the helical structure. The hyperchromic change is es-

(5) This is indicated by the sign of the optical rotatory change; see J. R. Fresco, *Tetrahedron*, **13**, 185 (1961).