Table 1. Rate of Cooling of Tektites

$T(t°)$ K	Cooling time (sec) from 10,000° K to $T(t°)$ K $r = 1$ cm	$r = 5$ cm
5,000	0·29	1·43
3,000	1·48	7·40
2,000	5·05	25·2
1,000	40·8	204
500	326·4	1,632

body after t sec. Solving this for the time required for a tektite of 1 cm radius and of 5 cm radius using the values $\rho = 2·4$ g/cm and $c = 0·21$ cal/g-mol. deg. (value from Grant quoted in ref. 7) gives the results shown in Table 1. Calculations by Prof. J. C. Jaeger (personal communication) show that if the effect of the finite thermal conductivity is taken into account, the figures in Table 1 are not significantly altered. Further, since the molten material is ejected from the impact site at velocities of several kilometres per second, heat shielding would not be expected to affect these figures significantly. The original fusion temperature was arbitrarily taken as 10,000° K for the purposes of calculation, and no implication as to the actual prevailing temperature is intended. In fact, this temperature was chosen because it is probably greater than the vaporization point of tektites. Thus the figures in Table 1 indicate that the rate of cooling from any temperature at which tektites could exist is so rapid that the presence of lechatelierite particles and the alkali elements does not preclude an ultra-high temperature origin for tektites.

It should be noted, however, that even the vaporization temperature of tektites does not necessarily put an upper limit on the temperature of their formation since they could be flash-melted well above this point without actually vaporizing. In the d.c. arc, operating at temperatures of 3,000°–8,000° C, minutes are required, rather than seconds, completely to volatilize milligram quantities of silicates. The data in Table 1 indicate that tektites weighing less than 200 g would have achieved a temperature of 3,000° K in less than 5 sec regardless of the original fusion temperature.

Although the extent of volatilization losses depends on the fusion temperature one assumes, it is not necessary to assume that vaporization temperatures have been achieved. It is well known to spectrographers that significant losses of the alkali elements occur within seconds of striking the d.c. arc at temperatures of 3,000° C[8].

These calculations do not, of course, give any evidence that tektites have in fact been subjected to ultra-high temperatures; but they indicate that such a possibility, with the concomitant implication of significant selective volatilization, must be seriously considered. Evidence that selective volatilization from tektites has occurred will be presented elsewhere.

We thank Prof. J. C. Jaeger for helpful discussions.

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[1] Lovering, J. F., *Nature*, **186**, 1028 (1960).

[2] Cohen, A. J., *Twenty-first Intern. Geol. Cong.*, Part 1, Sect. 1, 30 (1960).

[3] Menzel, D. H. (ed.), *Fundamental Formulas of Physics*, 2 (Dover Pub., Inc., New York, 1960).

[4] Barnes, V. E., *Geochim. et Cosmochim. Acta*, **14**, 267 (1958).

[5] Taylor. S. R., Sachs, M., and Cherry R. D., *Geochim. et Cosmochim. Acta*, **22**, 155 (1961).

[6] Cork, J, M., *Heat* (John Wiley and Sons, Inc., New York, 1933).

[7] Baker, G., *Mem. Nat. Mus. Victoria*, **23**, 1 (1959).

[8] Ahrens, L. H., and Taylor, S. R., *Spectrochemical Analysis*, second ed. (Addison-Wesley Pub. Co., Reading, Mass., 1960).

CHEMISTRY

Bimolecular Substitution in Octahedral Transition Metal Ions, and the Concept of Amphiphilicity

The problem of assigning mechanisms to certain octahedral substitution reactions has been complicated by two principal ambiguities. If the reacting complex has acidic protons on the non-participating groups, second-order kinetics resulting from substitution by basic anions may indicate either an S_N2 or an S_N1CB mechanism, and, in general, it is difficult to distinguish the two. With non-basic substituting anions or systems without extractable protons, first-order kinetics may indicate either an S_N1 mechanism or substitution involving preliminary bimolecular solvent intervention. The compound *cis*-*bis*-pyridino-*bis*-*o*-phenanthroline ruthenium II perchlorate, *cis*-[Ru phen$_2$ py$_2$] (ClO$_4$)$_2$, has no extractable protons, and therefore should give a unique answer to the first ambiguity; and it was hoped that dry solvent acetone would not engage in preliminary bimolecular substitution.

The following reactions were carried out under kinetically controlled conditions in dry acetone: *cis*-[Ru phen$_2$ py$_2$]$^{2+}$ + $X^- \rightarrow$ *cis*-[Ru phen$_2$ py X]$^+$ + py, where X = Cl, Br, I, NCS (nitrogen bonding), N_3, and NO_2. Using dry *o*-dichlorobenzene, the same substitutions were carried out, together with those of the extra two anions, OH^- and CN^-, but in less detail than the acetone reactions. In all cases the complex was introduced as the perchlorate and the anions as their tetraphenyl arsonium salts. Although ion-pair formation is likely between the positive and negative species in these solvents, there are good reasons for believing that this phenomenon does not greatly qualify the general conclusions in regard to the mechanisms which will be put forward here.

In acetone the anions Cl^-, Br^-, I^-, and NCS^- reacted by a first-order process; the rate depended only on the concentration of the complex and was independent of the nature and concentration of the anion. Moreover, for these four anions a mass-law retardation and ionic-strength acceleration were observed. The N_3^- and NO_2^- anions substituted at a rate which was dependent on the concentration of the complex and also on the nature and concentration of the anion; the NO_2^- anion substituted considerably faster than the N_3^- anion, the reaction of which in turn was much faster than the first-order reactions. At 100° C, the relative ratios (Cl^-, Br^-, I^-, NCS^-): N_3^- : NO_2^- of the rates was 1 : 4 : 9, and, furthermore, the activation energy of the NO_2^- reaction was 7 kcal less than that of the Cl^-, Br^-, I^-, and NCS^- reactions. A similar pattern was observed in *o*-dichlorobenzene, except that the OH^- anion substituted by a first-order process and at the same rate as the anions Cl^-, Br^-, I^-, and NCS^-, but CN^- substituted fastest of all the anions (including N_3^- and NO_2^-) by a second-order process. If optically active complex was used all the substitutions (independent of order) proceeded with complete retention of configuration.

These results are interpreted as follows: substitution by anions which proceed by a first-order process are unimolecular, and the second-order reactions are bimolecular. The anions therefore divide themselves mechanistically into two categories, and it is notable that only those anions (N_3^-, NO_2^-, and CN^-), which have potentially vacant p-orbitals for π-bonding,

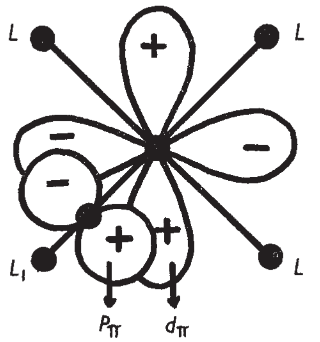

Fig. 1

engage in bimolecular substitution. The anions (Cl^-, Br^-, I^-, NCS^-, and OH^-), having no such orbitals sufficiently low-lying in energy, substitute by a unimolecular process. It seems plausible to conclude that vacated $p\pi$ orbitals of the incoming group are involved in the substitution process, and that the greater stability afforded to the incoming group by π-bonding is necessary to carry the bimolecular reactions through to completion.

A group which engages in a substitution reaction of the foregoing type, because it simultaneously donates and accepts electrons, may be called 'amphiphilic', and a bimolecular amphiphilic substitution reaction may be symbolized as S_A2. The nature of these bimolecular substitution reactions may be envisaged as follows. The incoming group attacks an octahedral edge and donates its lone pair of electrons to the highly positive ruthenium atom; at the same time a vacated $p\pi$ orbital on the donor atom of the incoming group accepts electrons from the filled $d\varepsilon$ subshell of the ruthenium. A plausible mode of donor π-orbital overlap is that illustrated in the diagram, in which the four ligands (L) are at the corners of the square, and two others (not shown) are above and below the plane.

The incoming ligand is situated at an octahedral edge and the $p\pi$ orbital overlaps laterally with the $d\varepsilon$ orbital the longitudinal projection of which is towards the outgoing ligand L_1.

In the system, *cis*-[Ru phen$_2$ py$_2$]$^{2+}$, it is likely that the pyridino groups are stabilized, to some extent, by $d\pi$—$p\pi$— double bonds. Experiment shows that simple σ-donors are ineffective as bimolecular substituting agents, but that groups which are both σ-donors and π-acceptors are effective. This seems to imply that, in the foregoing system, both ρ- and π-bonding is required to release the π-bonded pyridino groups from the complex by a bimolecular mechanism. In the bimolecular transition state of the foregoing reactions, the incoming and outgoing groups must share a $d\pi$ orbital, and thus, relative to the ground-state, the incoming group will be stabilized and the outgoing group be destabilized by the partial transference of the $d\pi$ bond to the incoming group. Therefore π-bonding in the transition state promotes both the bond making and the bond breaking components of this bimolecular mechanism.

In analysing the amphiphilic order of a series of reagents several electronic factors must be discussed, relating to the metal and ligand orbitals available. Probably the best single experimental criterion which embraces, to some extent, all these factors is the *trans*-effect in platinum II complexes. It is proposed that for a given charge series the amphiphilicity will follow the *trans*-effect in platinum II complexes. Amphiphiles with the strongest *trans*-effect will have the highest amphiphilic power. Arsines, phosphines and sulphides might be considered potentially amphiphilic reagents using empty $d\pi$ orbitals in the transition (and final) states. There are clearly others; but it is notable that the reagents used here do, in fact, follow the *trans*-effect series, that is, $CN^- > NO_2^- > N_3^- > NCS^-$, I^-, Br^-, Cl^-, OH^-.

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Absorption Correction in the Viscometry of Dilute Solutions of High Polymers

In a private communication, Drs. S. Gundiah and S. L. Kapur (of the National Chemical Laboratories, Poona, India) have pointed out to us that the derivation of the principal equation in our earlier communication[1] is in error, and that there is, because of this, a term missing from the equation. We acknowledge the error and are grateful to them for detecting it; but we wish to make it clear that the missing term should be negligible not only for the system we used as an example, but also for all systems of the type we specified, namely, "dilute solutions of high polymers". In this communication, then, we provide (*a*) a correction for the record and (*b*) additional evidence that the method we proposed is both sound and useful, and applicable to a wide variety of systems.

(*a*) The third paragraph of the earlier communication should be replaced by the following:

From this it follows that, in sufficiently dilute solutions:

$$\frac{t_{sp}}{c} = \left(1 + \frac{4a}{R}\right)[\eta] + k'\left(1 + \frac{4a}{R}\right)[\eta]^2 c + \frac{4a}{R} \cdot \frac{1}{c} \qquad (2)$$

and

$$\frac{\ln t_r}{c} = [\eta] - (\tfrac{1}{2} - k')\,[\eta]^2 c + \frac{4a}{R} \cdot \frac{1}{c} \qquad (3)$$

for in such solutions:

$$\frac{\ln t_r}{c} = \frac{\ln\,(1 + t_{sp})}{c} = \frac{t_{sp}}{c} - \frac{\tfrac{1}{2}\,(t_{sp})^2}{c} + \ldots$$

Subtracting (3) from (2), we obtain:

$$\frac{t_{sp}}{c} - \frac{\ln t_r}{c} = \frac{4a}{R}[\eta] + \left(\frac{1}{2} + k' \cdot \frac{4a}{R}\right)[\eta]^2 c \qquad (4)$$

In this equation, the term $4a/R\ .\ 1/c$ (the most significant of the absorption terms in equations (2) and (3)) does not appear. Moreover, the term $k'\ .\ 4a/R$ is, for high polymer systems, small compared with $\tfrac{1}{2}$. Equation (4) thus reduces to the simple equation:

$$\frac{t_{sp}}{c} - \frac{\ln t_r}{c} = \frac{4a}{R} \cdot [\eta] + \frac{1}{2}[\eta]^2 c \qquad (5)$$

and hence a value of $[\eta]$ that is unaffected by 'absorption' can be evaluated from the slope of the plot of:

$$\frac{t_{sp}}{c} - \frac{\ln t_r}{c} \text{ vs. } c$$