The form of $p(\eta, T)$ obtained in the previous section [Eq. (10)] is verified by the plots in Figs. 3(a)–3(c). The validity of Eq. (5) for τ_{enc} is assumed. The simple unimolecular reaction model is thus seen to account in a satisfactory way for the exchange probability parameter $p(\eta, T)$. Interestingly enough, it is empirically found that $J_0\tau_{enc}$ for radical–radical exchange is strongly solvent-dependent, and that for the same solvent (methyl cyclohexane) $J_0\tau_{enc} \gg J_0'\tau'_{enc}$. The values of $J_0\tau_{enc}$ are found to be $1.01\times10^3\,\eta/T$ (n-pentane), $2.81\times10^3\,\eta/T$ (propane), $\gtrsim1\times10^3\,\eta/T$ (methylcyclohexane), while $J_0'\tau'_{enc} = 0.19\times10^3\,\eta/T$ (methylcyclohexane). Viscosities are expressed in centipoise.

From the empirical values of $J_0\tau_{enc}$ and Eq. (5) with $\lambda = 3\times10^{-8}$ cm, J_0 was calculated to be 1.6×10^{11} sec^{-1} in n-pentane, 4.5×10^{11} sec^{-1} in propane and $\gtrsim1.6\times10^{11}$ sec^{-1} in methylcyclohexane. $J_0'\tau'_{enc}$ is

about an order of magnitude smaller than the corresponding quantity for radical–radical exchange. It is expected, however, that λ', the interaction radius for the oxygen molecule, is also appreciably smaller. These values of J_0 are about an order of magnitude larger than the value estimated by Pake and Tuttle[2] for polycrystalline DPPH (10^{10}–10^{11} sec^{-1}).

Crystal Structure of Li₆BeF₄ZrF₈†

D. Richard Sears and John H. Burns

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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The crystal structure of Li₆BeF₄ZrF₈ has been determined by x-ray diffraction. The tetragonal unit cell, having $a = 6.57$, $c = 18.62$ Å, contains four formula weights; the space group is $D_{4h}^{19}-I4_1amd$. Discrete BeF₄²⁻ and ZrF₈⁴⁻ ions are connected by shared Li⁺ ions. The BeF₄²⁻ tetrahedron is quite regular with a Be–F distance of 1.57 ± 0.01 Å; the ZrF₈⁴⁻ dodecahedron has two independent Zr–F bonds of 2.05 ± 0.01 Å and 2.16 ± 0.01 Å, and deviates considerably from the shape predicted by theory.

INTRODUCTION

ZIRCONIUM is known to occur as the central atom of a variety of complex coordination polyhedra, often bearing eight ligands arranged in dodecahedral or square-antiprismatic symmetry.[1,2] Racah[3] and Duffey[4] have derived orbital strengths for these configurations using d^4sp^3 hybridization. Their calculations established no significant energy difference between the configurations, if isolated complexes are considered.

The configuration adopted in a particular crystal is therefore determined in part by external influences, such as ligand–ligand repulsions, constraints due to

bonding between ligands, and packing requirements. Thus it is interesting to examine MX_8-type configurations in which, as in the well known Mo(CN)₈⁴⁻ ion,[5] the central metal atom is bonded to eight apparently equivalent monodentate ligands.

In an investigation of the phase diagram of the ternary system LiF–BeF₂–ZrF₄, Thoma *et al.*[6] discovered a primary phase of composition 6LiF·BeF₂·ZrF₄. The stoichiometry and preliminary x-ray studies suggested the possible occurrence of complex octafluorozirconate and tetrafluoroberyllate ions in the crystal.

The coexistence of two discrete complex anions in a crystal is not common. But since it seemed likely in this compound, a crystal-structure analysis was carried out to examine in detail the configuration of the discrete

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