rate of thermolysis of **1** (in CD_3CN without **7**) to **2**: k at 110.1° = $(3.4 \pm 0.2) \times 10^{-4}$ sec^{-1}, k at 90.6° = $(4.2 \pm 0.2) \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 29$ kcal/mol, $\Delta S^{\ddagger} = 1$ eu. With **7** all of **1** was converted into the adducts described by LeGoff, *et al.*,[10] but in the presence of 2 mol of a weaker dienophile, maleic anhydride, **1** provided **2** and maleic anhydride adducts of **4** in 40 and 60% yield, respectively, although the rate of decrease of **1** remained the same as k_1 (110°). Therefore, we conclude that tetracyanoethylene and maleic anhydride simply intercept intermediate **4**, the latter less efficiently, and that path a is the rate-determining step of the thermolysis of **1**.

Acknowledgment. We thank the National Research Council of Canada and the donors of the Petroleum Research Fund (administered by the American Chemical Society) for financial support.

H. H. Westberg, E. N. Cain, S. Masamune
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada
Received October 6, 1969

Fluorescence of Acetone in the Solution Phase

Sir:

The recent report by O'Sullivan and Testa on the fluorescence of acetone excimer and monomer species has created interest in this laboratory, since the gas-phase fluorescence of 2-pentanone[2] has a spectral distribution similar to that which O'Sullivan and Testa attribute to the excimer of acetone. Thus, there exists a possibility that the 2-pentanone emission at 25 Torr is actually due to an excimer. In the process of initiating experiments to study the gas phase emission as a function of pressure we have repeated the O'Sullivan and Testa experiments in the solution phase. As a result of these experiments we conclude that the apparent monomer emission (λ_{max} 345 nm) reported by those workers appears to be due to an impurity in the acetone, whose fluorescence is quenched by acetone in the high acetone concentration region ($\sim 10^{-2}$ M).

The fluorescence spectra at varying concentrations of acetone in hexane are shown in Figure 1.[3] The spectra were obtained with a Farrand spectrofluorometer using slits with a 5-nm bandpass. The acetone was "spectroquality" and was purified by preparative gas chromatography just prior to use. The hexane used was a fresh bottle of either spectroquality or chromatoquality (Matheson Coleman and Bell). If a bottle of either grade hexane was used which had been opened several times previously during normal laboratory use, spectra similar to those reported by O'Sullivan and Testa were obtained. However, the short wavelength emission was at 330 nm rather than 345 nm and was more intense than that seen by O'Sullivan and Testa.[4] Careful distillation of this hexane removes the 330-nm emission. It was observed that if the hexane came in contact with plastic stoppers on volumetric flasks or rubber serum caps, the emission at 330 nm was very intense at low ketone concentrations.

Experiments using distilled water and carefully distilled methanol as solvents showed only the 405-nm emission and the concentration dependence agreed with that shown in Figure 1. Experiments with chromatographically purified diethyl ketone gave only the 405-nm emission at concentrations of $\geq 3 \times 10^{-4}$ M.

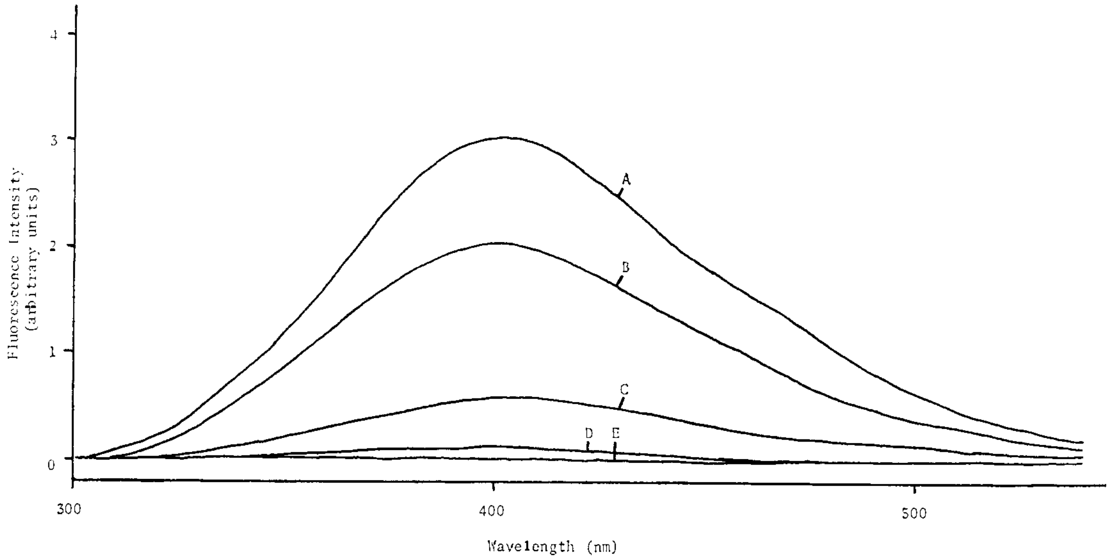

Figure 1. Fluorescence spectra of acetone at varying concentrations (hexane solvent, excitation λ 2850 ± 50 Å): (A) 2.2×10^{-2} M, (B) 1.1×10^{-2} M, (C) 2.7×10^{-3} M, (D) 2.7×10^{-4} M, (E) pure hexane.

A plot of the integrated area under the spectral curve *vs.* acetone concentration was linear to 0.03 M acetone, beyond which the integrated intensity showed the char-

---

(1) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 6245 (1968).

(2) F. S. Wettack, *J. Phys. Chem.*, **73**, 1167 (1969).

(3) Professor N. J. Turro's group at Columbia has obtained similar spectra. We thank Mr. J. C. Dalton for communicating these unpublished results to us.

(4) Private communication with Professor Testa indicates that the 330-nm emission seen in our work is definitely not the same as the 345-nm emission seen in their work. The solvents employed by O'Sullivan and Testa were emission-free and, hence, we conclude that the short-wavelength emission seen by those workers was probably due to an impurity in the ketone. We thank Professor Testa for helpful discussions on this matter.

acteristic "inner filter effect" discussed by Ellis.[5] One characteristic of excimer emission is a quadratic dependence on concentration. The linear dependence found in this work is a further piece of evidence that the 405-nm emission is not that of an excimer.

From the above experiments we conclude that the emission attributed to an acetone monomer by O'Sullivan and Testa is due to an impurity, and that the emission at 405 nm is the true acetone monomer fluorescence. As a result, we conclude that the gas-phase emission of 2-pentanone is most likely due to a monomer species.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation for partial support of this work. Funds from the National Science Foundation and E. I. du Pont de Nemours and Company were used to purchase the spectrofluorometer. Discussions with a number of our colleagues at Hope College are gratefully acknowledged.

---

(5) E. W. Ellis in "Fluorescence and Phosphorescence Analysis," D. M. Hercules, Ed., Interscience Publishers, New York, N. Y., 1966, Chapter 2.

Gordon D. Renkes, F. Sheldon Wettack
Department of Chemistry, Hope College
Holland, Michigan 49423

Received September 9, 1969

Metal Ion–Aromatic Complexes. IX. The Structure of a Seven-Coordinate Tin(II)–Benzene Complex, $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$

Sir:

In an earlier communication[1] we reported the preparation and characterization of the remarkable and previously unknown compounds $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$, $(C_6H_6)_2 \cdot Pb(AlCl_4)_2$, $C_6H_6 \cdot 2TlAlCl_4$, $(C_6H_6)_2 \cdot TlAlCl_4$, and $C_6H_6 \cdot BiCl_2AlCl_4$. All the available evidence at that time (infrared, Mössbauer, nmr) pointed to a highly symmetrical structure for $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$ (most likely a D_{6h} ferrocene type). To establish unambiguously the molecular stereochemistry of this Sn compound, we undertook the solution of the crystal structure and found an unexpected pentagonal bipyramid seven-coordinate Sn(II).

A diffraction quality single crystal 0.65 × 0.35 × 0.80 mm was coated with Vaseline and sealed in a thin-walled glass capillary. The crystal was mounted with the long direction, [101], approximately parallel to the ϕ axis on the Picker diffractometer, and aligned by well-known methods.[2] A least-squares fit of the χ, ϕ, 2θ, and ω angles of 25 carefully centered reflections[2] gave the crystal parameters with Mo Kα radiation (λ 0.71068 Å): $a = 11.300(2)$, $b = 17.355(8)$, $c = 12.655(6)$ Å, and $\beta = 110.04(1)°$, $P2_1/n$.[3] With $Z = 4$, $\rho_{calcd} = 1.84$ g cm^{-3}, $\rho_{obsd} = 1.76$–2.01 g cm^{-3} in a CCl_4–CBr_3H mixture; μ was calculated to be 26.2 cm^{-1} with Mo Kα. No corrections were made for absorption since there is invariably some decomposition product coating the crystal, and this absorption plus the effect of the capillary and Vaseline collectively probably outweigh simple crystal absorption effects. Peaks were scanned at 1°/min for 144 sec and backgrounds were estimated at ±1.2° 2θ of peak maxima by stationary counting for 40 sec. By this means 3430 independent *hkl* planes were measured for $2\theta < 70°$. The integrated intensity was calculated from $I(\text{net}) = I(\text{scan}) - 1.40(B_1 + B_2)$. The reflections were considered nonzero if $I(\text{net}) > 2.5[1.40(B_1 + B_2)^{1/2}]$. By this criterion 1346 reflections were retained. The structure was solved by conventional heavy atom methods[4] and refined by full matrix least squares[5] with weights determined from intensity statistics and a 4% intensity factor,[6] to a final R of 0.063[7] and weighted R of 0.076.

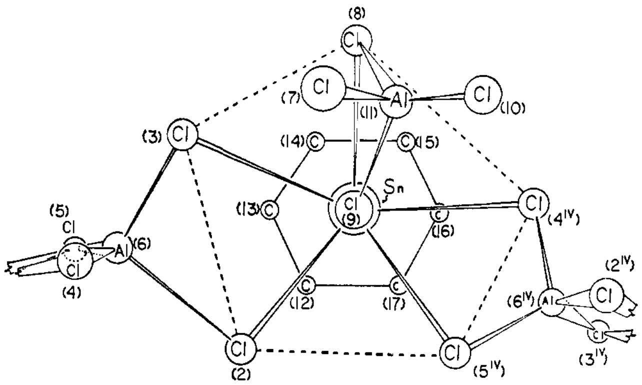

Figure 1. Idealized view of the $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$ complex showing the seven-coordinate pentagonal bipyramidal Sn(II). The view is down the axial Cl which is superposed on the Sn atom. The chain is built up by Cl(4) and Cl(5) bonded to an adjacent Sn(II) to the left, and Cl^{IV}(3) and Cl^{IV}(2) bonded to an adjacent Sn(II) to the right. The dotted lines define the pentagonal plane.

The gross structure features of $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$ may be described by a Sn(II) moiety bonded to two chlorine atoms from each of three different $AlCl_4^-$ ions (sharing of tetrahedral edges with Al), to form a linear chain structure propagating in approximately the [111] direction. The Sn(II) polyhedron is completed by a symmetrical axial coordination to one of the benzene rings that may be considered to be lying on the surface of the chain. The benzene rings of adjacent chains are back to back. However, the second aromatic entity lies in a cleft between chains and should be regarded as a molecule of solvation. This arrangement of $AlCl_4^-$ units and benzene about Sn(II) gives the metal a coordination number of seven in an approximate pentagonal bipyramid geometry. This geometry assumes the benzene fills only one axial coordination site (Figure 1). It is to be noted that Sn(II) is essentially tris-chelated by $AlCl_4^-$ anions.

---

(1) Th. Auel and E. L. Amma, *J. Amer. Chem. Soc.*, 90, 5941 (1968).

(2) (a) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1967; (b) K. Knox in "Master Card Program for Picker Four-Angle Programmer," Picker Instruments, Cleveland, Ohio, 1967, p 11; (c) W. R. Busing and H. A. Levy, *Acta Cryst.*, 22, 457 (1967).

(3) "International Tables for X-Ray Crystallography," Vol. 1, N. F. M. Henry and K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1962.

(4) Patterson and electron density calculations performed on an IBM 7040 with ERFR-3 program, a modification of ERFR-2 of Sly–Shoemaker–Van den Hende by D. R. Harris.

(5) Least-squares refinement performed with ORFLS of W. Busing, K. O. Martin, and H. A. Levy (ORNL-TM-305, 1962) with local modifications. Scattering factors and other computer programs used are to be found in M. S. Weininger, J. E. O'Connor, and E. L. Amma, *Inorg. Chem.*, 8, 424 (1969).

(6) S. W. Peterson and H. A. Levy, *Acta Cryst.*, 10, 70 (1957).

(7) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = \{\Sigma\omega[|F_o| - |F_c|]^2\}^{1/2}/[\Sigma\omega F_o^2]^{1/2}$.