

CHEMISTRY

Chairman: QUENTIN R. PETERSEN, Wabash College

ABSTRACTS

KENNETH COOK, Anderson College, was elected chairman for 1965

The Dissociation of BH_3CO into BH_3 and CO . T. P. FEHLNER and W. S. KOSKI, University of Notre Dame.—The decomposition of BH_3CO has been studied in a low pressure flow system using a special mass spectrometer. The products, determined by using low energy electrons, were found to be BH_3 and CO only. These products were shown to originate in the reactor. As recombination was not a problem at the low reactor pressures, the simple reaction



was being observed. The calculated first order rate constant, obtained by following the loss of BH_3CO , was found to be independent of the BH_3CO partial pressure, the total pressure, and the surface of the reactor within the experimental range of variables. The mole fraction of BH_3CO ranged from 0.05 to 0.6, while the total pressure was varied from 1 to 20 microns. Three different surfaces were employed. The average rate constant was found to be 19 sec^{-1} at 400°K . Because of the low pressure employed, it was not possible to obtain an activation energy for the reaction from the temperature variation of the rate constant. It was found possible, however, to estimate the activation energy from the determination of the rate constant at 400°K by using the frequency factor for this unimolecular reaction which had been determined in a previous kinetic study. It was found that a good estimate of the activation energy is $23.1 \pm 2 \text{ kcal/mole}$. Neglecting the activation energy for the recombination reaction, this gives $D(\text{H}_3\text{B}-\text{CO}) = 23.1 \pm 2 \text{ kcal/mole}$. This value when combined with equilibrium data yields $D(\text{H}_3\text{B}-\text{BH}_3) = 37.1 \pm 4 \text{ kcal/mole}$.

The Use of Three Disc Electrode Configurations in Electroanalytical Diffusion Coefficient Measurements. JOHN F. ZIMMERMAN, Wabash College.—Chronopotentiometric and chronoamperometric studies have been performed at a shielded gold electrode, a planar unshielded platinum disc, and a similar disc configuration (carbon paste electrode) fashioned from an intimate mixture of carbon and mineral oil. The electrode configurations were studied by examining the Ag(I) reduction in 0.1 M KNO_3 , the ferrocyanide oxidation in 2 M KCl , and 3,3'-dimethoxybenzidine oxidation in $0.5 \text{ M H}_2\text{SO}_4$. Observations at both unshielded electrodes had to be limited to periods less than sixty seconds. Positive deviations were noted at longer time intervals. This was attributed to the increasing importance of convective interference in the semi-infinite linear diffusions (SILD) mode of mass transport. The SILD approximation was valid for twenty minutes at the shielded electrode. The "break potential" method of analyzing the chronopotentiometric wave was found to be the method of analysis in best agreement with the chronoamperometric data.

¹Research done at the Chemistry Department of The Johns Hopkins University, Baltimore, Maryland.

Reaction of Decachloropentacyclo (5.3.0.0^{2,6}.0^{3,9}.0^{4,8}) decan-5-one and Some Derivatives. E. T. MCBEE, T. B. WIELICZKO and C. J. MORTON, Purdue University.—This work represents the first reported example of the linking of two decachloropentacyclodeca units. The reaction of decachloropentacyclo (5.3.0.0^{2,6}.0^{3,9}.0^{4,8}) decan-5-one with methylmagnesium iodide gave 5-methyl-1,2,3,4,6,7,8,9,10,10-decachloro (5.3.0.0^{2,6}.0^{3,9}.0^{4,8}) 5-decanol. This did not react with phosphorus pentachloride but with thionyl chloride gave a compound whose structure consisted of two decachloropentacyclodeca units linked by a sulfite bridge. The mechanism of this reaction is discussed.

Resonance Transfer of Excitation in Viscous Media. RICHARD J. POVINELLI, PETER K. LUDWIG and MILTON BURTON, University of Notre Dame.—Quenching of fluorescence (excited in this work by 3030 Å uv light) of *m*-terphenyl (*m*-TP) by 9, 10-diphenylanthracene (DPA) and 9, 10-dibromoanthracene (DBA) respectively in benzene-paraffin oil solutions, studied as a function of viscosity, gives information about the relative importance of collisional and resonance energy transfer. The choice of system is based on the fluorescence decay times and the overlap characteristics of the emission spectrum of *m*-terphenyl and the absorption spectra of the anthracene derivatives acting as quenchers. For the systems *m*-TP/DBA and *m*-TP/DPA, theoretical critical transfer distances R_0 of 27.9 Å and 29.9 Å respectively were found. The corresponding experimental values are 37.4 Å and 40.3 Å. From Stern-Volmer plots, quenching constants γ were determined and compared to those obtained with CCl_4 as quencher. (Presumably, with CCl_4 as quencher, collisional quenching alone occurs.) γ values vary between 289 and 185 M^{-1} for *m*-TP/DBA and 320 to 235 M^{-1} for *m*-TP/DPA in the viscosity range 0.606 to 22.3 cp. For *m*-TP/ CCl_4 , γ values are 14.6 M^{-1} (viscosity = 0.606 cp) and 4.5 M^{-1} (viscosity = 12.1 cp). The differences in the two sets of γ values point up the differences in mechanism of excitation transfer.

Luminescence Phenomena at 77°K and 90°K. MICHEL A. DILLON, PATRICK J. HERLEY and MILTON BURTON, University of Notre Dame.—Luminescence of long duration in pure 3-methylpentane glass at 77°K consequent to irradiation by ^{60}Co γ rays has been previously reported from this Laboratory. As a matter of convenience, new work has been performed additionally with 2-methylpentane. The wavelength of light emission extends over about 1500 Å with $\lambda_{\text{max}} \approx 4250$ Å as determined by rapid scan spectrophotometry. The new observations here reported relate exclusively to light emission in the range 4200 - 4300 Å. As in previously reported work, the isothermal decay (i.e., the very fast decay portion) of the light emission was found to obey an equation represented by a sum of three exponentials with lifetimes of order of 500 sec but the faster decay constants differ markedly from those previously reported. Values of activation energies were obtained from isothermal decay curves on samples irradiated and permitted to decay at 77°K and 90°K respectively. The activation energy so determined for both 2- and 3-methylpentane now appears to be 0.03 eV for all such portions. The entropy of activation for the fast portion of 3-

methylpentane is now estimated to be 46 e. u. Decay is accelerated by continuous irradiation with light of $\lambda > 7000$; as in the dark experiments, the decay curve breaks into three portions but the rate constants (particularly the initial one) are significantly increased without any apparent effect on E_a or ΔS^\ddagger . The observed phenomena are explained in terms of an electron-hole recombination model with the charge separation being the result of the initial energy deposition.

Radiolysis of Benzene and Benzene-Cyclohexane Mixtures in the Presence of Nickel Tetracarbonyl. HELMUT F. BARZYNSKI, ROBERT R. HENTZ, and MILTON BURTON.—*G* values of hydrogen and biphenyl formation in γ irradiated mixtures of benzene and nickel tetracarbonyl show that some excited benzene species are protected against decomposition by nickel tetracarbonyl. It is argued that two kinds of primary process contribute to the hydrogen yield: (1) a rapid unimolecular elimination of molecular hydrogen that is not quenched by carbonyl; (2) a process giving a second-order hydrogen yield that is associated with biphenyl formation and is quenched by carbonyl. Yields were determined for the major radiolysis products from benzene-cyclohexane mixtures containing nickel tetracarbonyl at fixed electron fraction (ϵ 0.68) at different electron fractions of each hydrocarbon in the range ϵ 0 to 0.32. At ϵ (nickel tetracarbonyl) 0.68 most of the cyclohexane decomposition is inhibited; the residual decomposition of the cyclohexane is to a major extent by rearrangement to ultimate molecules and to a minor extent by rupture into free radicals and atoms. These residual decomposition processes are not appreciably quenched by further addition of either protective agent. The suppression of products by benzene, in this case, represents actual scavenging of free radicals and atoms.

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