

CHEMISTRY

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ABSTRACTS

Out-of-Plane Bending Force Constants of Carbonium Ions: A Novel Suggestion Explaining Fast Solvolysis Rates without Invoking Non-classical Ions. A. J. MCELHENY and R. E. DAVIS, Department of Chemistry, Purdue University.—Detailed quantum mechanical calculations have been made on methyl cation, CH_3^+ , as a function of the HCH angle in the plane and the H- CH_2 angle out-of-the-plane. Evidence is presented that the out-of-plane force constant of the C-H bond goes through a minimum when the angle of the other HCH unit is 90° . The out-of-plane force constant of the C-H bond is then compared with the out-of-plane force constant of $\text{O} = \text{CH}_2$.

It is suggested from these data that fast carbonium reactivity usually observed with strained compounds can be explained using force constant changes rather than invoking nonclassical resonance structures. Thus the qualitative reasons of H. C. Brown in rejecting the nonclassical concept, has very strong theoretical foundation.

Studies on the Willgerodt Reaction. IV. The Kinetics of Isomerization of 1,3-Diphenyl-2-propanone by Sulfur and Morpholine. R. E. DAVIS and Miss CYNTHIA T. THEISEN, Department of Chemistry, Purdue University.—A kinetic study is reported on a Willgerodt reaction. The reaction is first order in ketone and first order in sulfur. Although the kinetic data reported in this paper are limited, the data are such that they disprove every single mechanism previously published. In keeping with the serious critique, no new mechanism is suggested, however. Recent work on the Willgerodt reaction demonstrates that the system of an amine, ketone and elemental sulfur is an extremely complex mixture. The nature of the mixture has only been recently appreciated.

Ultraviolet Absorption Spectra of Some 1,3-Bisaryl-2,4-uretidinediones and Trisaryl-*s*-triazine-(1H,3H,5H)2,4,6-triones. LEROY A. MCGREW and DAVID STIBBINS, Ball State University.—The ultraviolet absorption characteristics of the title compounds were determined in ethanol solution in the wavelength region 340-200 millimicrons. The spectra of both types of compounds were characterized by two absorption maxima. The primary band occurred in the region 200-210 millimicrons, and a secondary band was observed in the region 250-270 millimicrons. The ratio of molar absorptivities, e_2/e_1 for the secondary and primary bands fell in the range 0.42-1.17 for the uretidinediones and in the range 0.07-0.21 for the *s*-triazinetrienes. This difference in ratio may be used as a means of differentiating between the two types of compounds. The spectra of substituted aryl derivatives showed that the positions of the absorption maxima were insensitive to the presence of auxochromic

groups. Spectra of the title compounds were compared to the spectra of selected acyclic model compounds and found to be similar.

Catalyst and Substituent Effects in the Dimerization and Trimerization of Aryl Isocyanates. LEROY A. MCGREW, Ball State University.—The polymerization reactions of substituted aryl isocyanates were studied using tributylphosphine and triethylamine catalysts. The phosphine catalyst caused formation of cyclic isocyanate dimers if no *ortho* substituent was present, while the amine catalyst caused cyclic trimer formation. The presence of a ring substituent in an *ortho* position, or of a nitro group in any position, prevented dimer formation, and trimers were observed to form with either catalyst. The various dimers and trimers were characterized by their infrared and ultraviolet spectra, and by the selective cleavage of the dimer ring by secondary amine bases. These results were correlated with ionic mechanisms in which the dimerization was conceived to be a rapid, unfavorable equilibrium, with trimerization being a slower, irreversible process.

Dehydration of 3-Hexen-2,5-diol. Evidence for alpha-Protonation of an Aliphatic, Conjugated Dienol. HARRY MORRISON and STEVE KUROWSKY, Department of Chemistry, Purdue University.—Acid-catalyzed dehydration of 3-hexen-2,5-diol leads to the formation of 4-hexen-2-one, with only small amounts of the conjugated isomer produced. Dehydration in deuterophosphoric acid/deuterium oxide results in the formation of 4-hexen-2-one deuterated at the methylene carbon but not at the vinyl positions. Possible mechanisms for the formation of the unsaturated ketone are discussed and it is shown that the experiments in deuterated media require the postulate of protonation exclusively at the alpha position of 2,4-hexadien-2-ol.

The Shock Histories of Iron Meteorites and Their Implications. RALPH R. JAEGER¹ and MICHAEL E. LIPSCHUTZ, Departments of Chemistry and Geosciences, Purdue University. It has been found that shock pressures in excess of 130,000 atm. (130 kb) induce effects in iron meteorites (octahedrites) which can be detected by metallography and X-ray diffraction analysis. Of 65 iron meteorites, 63 have had their trace amounts of gallium and/or germanium measured and 46 have had their cosmic-ray exposure ages determined by other workers.

There is a correlation between shock history, Ga-Ge content and exposure age. The unshocked meteorites seem randomly distributed both with respect to trace element content and cosmic-ray exposure age. The shocked meteorites, on the other hand, are heavily quantized both with respect to gallium and germanium contents, and exposure ages. These correlations, together with ancillary observations, suggest the following conclusions:

- (1) About half of all iron meteorites reaching Earth have been shocked, in preterrestrial collisions, to pressures above 130 kb.
- (2) Most of the shocked iron meteorites were produced in a single collision 650 ± 60 million years ago.

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- (3) One of the partners to this collision seems to have been an asteroid whose initial orbit was largely, if not entirely, within the Asteroidal Belt. Its metallic portions had gallium and germanium contents corresponding to those of Group III (a standard geochemical classification for one of the gallium-germanium classes of iron meteorites).
- (4) The more massive partner may have been the parent of a majority of the stony meteorites. Its initial orbit possibly crossed that of Mars.
- (5) The collision resulted in the injection of meter-sized stony fragments into orbits crossing that of Mars.
- (6) Gravitational forces exerted by Mars resulted in the continuous injection of iron material into orbits crossing that of Earth, at least over the last million years.
- (7) Gravitational forces together with effects of secondary collisions resulted in the injection of stony material into Earth-crossing orbits.

The Mechanism of Hydrogen Formation in the γ -Radiolysis of 1, 4-Dioxane. MILTON BURTON, ROBERT R. HENTZ and WARREN V. SHERMAN, Radiation Laboratory,¹ University of Notre Dame.—A study has been made of the mechanism of formation of molecular hydrogen from cobalt-60 gamma-irradiated 1, 4-dioxane. It was found that the yield of hydrogen from carefully dried dioxane (1.4 molecules per 100 ev absorbed) is significantly smaller than reported previously by other workers. However, a progressive increase in yield was observed in the presence of increasing initial concentrations of water. The mechanism suggested to explain these results is that in pure dioxane combination of the radiolytically-produced ion-electron pairs is a very inefficient process for hydrogen formation. However, with water present, proton transfer from the dioxane cation to water can precede charge neutralization such that the previous neutralization process is replaced partially by one involving the hydronium ion and the electron. This results in the formation of hydrogen atoms and subsequently hydrogen molecules (by abstraction from the solvent). The enhancement of the hydrogen yield from dry dioxane by other proton acceptors (methanol, ammonia) and the lack of sensitivity to electron scavengers (nitrous oxide, iodine) support the proposed mechanism, as does the observation that the enhanced hydrogen yield in the presence of a proton acceptor can be depressed by addition of an electron scavenger prior to irradiation.

The Mechanism of Radiation-Induced Luminescence from Scintillators in Cyclohexane. MILTON BURTON, ROBERT R. HENTZ and RONALD J. KNIGHT, Radiation Laboratory,² University of Notre Dame.—Studies of radiation-induced luminescence from scintillators in various solvents

¹The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-570.

²The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-569.

have shown that different mechanisms are involved in aromatic and alkane solvents. It has been established that scintillator luminescence in benzene solutions occurs via energy transfer from the $1B_{2u}$ state of the solvent to the scintillator. A corresponding mechanism for cyclohexane solutions is precluded by lack of evidence for a cyclohexane excited state of sufficient lifetime to participate in such an energy-transfer process. Recent work on the role of transient ion pairs in the radiation chemistry of alkane solutions suggests their involvement in the mechanism of radiation-induced luminescence from scintillators in alkane solutions. To test such a mechanism, a number of solutes characterized by previous work as electron scavengers were added to scintillator solutions in cyclohexane. The solutes chosen did not quench luminescence excited by direct absorption of uv light in the scintillator but did quench the luminescence induced by ^{60}Co γ irradiation. A correlation was established between quenching in the γ -irradiated scintillator solutions and suppression of $G(N_2)$ in $10^{-2} M$ N_2O solutions in cyclohexane. Such a correlation implicates the electron as a precursor common to both effects. It is proposed that excitation of the scintillator results from neutralization of its anions or cations which are formed by electron capture or positive charge transfer, respectively.

Molecular Beam Scattering Technique and the Theory of Chemical Reactions. C. R. MUELLER, Purdue University.—The molecular beam technique will be discussed with special emphasis on its implication on the theory of reaction rates and the lack of evidence for the activated complex. The quantum mechanical nature of the collision process will be emphasized. Specific quantum effects in chemical kinetics will be shown on the basis of a model which enables one to predict reactive cross-sections and scattering fine structure.

Ultraviolet Absorption Spectra of the Isomeric Naphthobenzothiophene and Naphthobenzofurans. E. CAMPAIGNE and S. OSBORN, Chemistry Laboratories of Indiana University.—Synthetic methods for the convenient preparation of the three possible isomers of the isomeric naphthobenzothiophenes, naphtho[2,1-b]benzothiophene, naphtho[1,2-b]benzothiophene and naphtho[2,3-b]benzothiophene, are described. Similar methods lead to the formation of the oxygen analogs of these compounds, the naphthobenzofurans.

The ultraviolet absorption spectra of the above compounds are shown to be characteristic, and sufficiently different to permit their use in identification of the different isomers. Comparisons will be made between these compounds and the analogous nitrogen (benzocarbazoles) and carbon (benzofluorenes and tetracyclic aromatic hydrocarbons) compounds. The spectra of the related analogs are very similar, with bathochromic shifts in the principal maxima related to ability of the respective atoms or groups (-O, CH_2 , -S-, NH, -CH=CH-) to release electrons to aromatic resonance.

The Synthesis of Matatabiether and Related Terpenes. JOSEPH WOLINSKY and DAVID NELSON, Purdue University.—*Actinidia polygama*, a silver vine found in the Far East and known in Japan as Matatabi, is

of considerable interest because it is attractive to felines and certain insect species. Professor Sakan and his collaborators have isolated a variety of methylcyclopentane terpenes from the plant (cf. T. Sakan, J. Wolinsky, et al., 1965, *Tetrahedron Letters* 4097) and have shown that the lactone fraction is attractive to cats, whereas the ether and alcohol fractions lure a species of lacewing. In this paper we describe the synthesis of 4 of the insect attractants.

Exchange on Gas-Chromatographic Columns. M. A. WECHTER and F. SCHMIDT-BLEEK, Department of Chemistry, Purdue University.—We have recently observed a distinct correlation between dissociation energies (as a "bulk" physical parameter) and the ease of elemental and/or isotopic exchange of halogens on the surface of gas chromatographic columns. Data are presented and discussed in terms of a) exchange reaction mechanisms b) the exchange probabilities with respect to physical parameters.

Other papers read

Computers in Chemistry. HARRISON SHULL, Indiana University (by invitation).

Application of Vapor Phase Electron Diffraction to the Question of Aromaticity in 1,6-Methano-2,4,6,8,10-cyclodecapentane. LAWRENCE K. MONTGOMERY and J. COETZER, Indiana University.

Cis, Cis-Triaminocyclohexane and Some of Its Complexes. R. A. D. WENTWORTH and JOHN FELTON, Indiana University.

Structural Studies by X-ray Diffraction. R. O. SCHAEFFER, Indiana University.