

Urea has a resonance energy of approximately 41 kcal.,²⁸ and at least in the solid state is a completely planar molecule.²⁹ This planarity is destroyed when the activated complex is formed. Thus the activation process should require enough energy to compensate for the loss of resonance energy involved in activated complex formation. This resonance energy loss will be given by the difference in resonance energy between reactant and complex. If it is assumed that the activated complex involved in the urea decomposition possesses resonance energy approximately equal to that of an alkyl isocyanate, *i.e.*, about 8 kcal.²⁸; then the loss in resonance energy should be $41 - 8 = 33$ kcal.³⁰

(28) Ref. 18, p. 116. Ref. 7, p. 100, gives 33 and 30 kcal. Ref. 23, p. 138, gives 37 kcal.

(29) E. R. Andrew and D. Hyndman, *Disc. Faraday Soc.*, **19**, 195 (1955).

(30) Use of the other values²⁸ for resonance energies of urea and the alkyl isocyanates gives these values for the loss in resonance energy: 40 and 37 kcal. (based on ref. 7), 30 kcal. (based on ref. 23).

This value compares favorably with the 32 kcal. activation energy reported for the decomposition of urea in aqueous solutions (Table I).

Resonance energies for thiourea and the thiourea derivatives are not available, but some qualitative observations can be made. It seems reasonable to assume that methylation should destroy planarity and decrease the resonance energy. The lowered activation energies of *unsym*-dimethylthiourea and trimethylthiourea might be rationalized on this basis. In the absence of resonance energy data for these compounds, however, rigorous comparisons cannot be made.

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Electron Spin Resonance Spectra of the Anions of Benzene, Toluene and the Xylenes¹

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The preparation and electron spin resonance spectra of the anions of benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene are reported. The distribution of spin density is compared with predictions of molecular orbital theory.

Introduction

Although the reaction between alkali metals and hydrocarbons has been known for some time, only recently has it been shown to involve the transfer of one or two electrons from the alkali metal to the hydrocarbon.³⁻⁶ The scope of this reaction apparently includes all aromatic hydrocarbon systems of two or more conjugated rings. Until recently the only examples of single ring aromatic systems forming negative ions were those of nitrobenzenes.³ The preparation of benzene negative ion at room temperature was reported by Paul,⁷ but confirmation of his experiment has not been obtained.

Experimental Procedure

All samples were prepared under high-vacuum conditions by techniques similar to those described by Paul, Lipkin and Weissman.⁹ A typical preparation proceeded as follows. After the alkali metal had been distilled to form a mirror at the bottom of the apparatus, about 2 ml. of dimethoxyethane and 0.1 ml. of hydrocarbon were distilled

onto the metallic film. With the contents frozen, the sample tube was sealed from the vacuum system and warmed in a Dry Ice-acetone bath.

As the sample warmed and melted the characteristic color of the hydrocarbon anion formed at the surface of the metal and gradually diffused throughout the solution. The reaction proceeds rather rapidly with benzene and toluene, more slowly with the xylenes. On warming from -80° , these solutions gradually lose their color with accompanying formation of fine grey precipitates. At room temperature the solutions have a yellow to orange color whose intensity increases with time of contact between solution and metal. The yellow and orange solutions are not paramagnetic. Recooling the solutions restores the anion color as well as the paramagnetism.

Dimethoxyethane alone in contact with potassium at -80° yields a deep blue solution.⁸ The color fades with precipitation of metallic potassium at room temperature. The deep blue solution exhibits a weak spin resonance absorption line about two oersteds in breadth.

E.S.R. Observations and Discussion

The e.s.r. absorption spectra were taken on a spectrometer operating at approximately 9,000 Mc./sec. The magnetic field was modulated at 90 cycles/sec. Low temperatures were obtained by boiling liquid nitrogen and conducting the cold gas through a transfer tube into a sleeve dewar in the resonant cavity. The temperature in the cavity was controlled by regulating the boiling rate of the liquid nitrogen.

The spectrum of benzene negative ion consists of seven equally spaced lines with interval between lines 3.75 oersteds and intensity ratios approximately 1:6:15:20:15:6:1. The pattern corresponds to splitting by six equivalent protons. The

(8) Similar observations have been reported by J. L. Down, J. Lewis, B. Moore and G. Wilkinson, *Proc. Chem. Soc.*, 209 (1957).

(1) This work was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract AF 18(600)-1133. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

(2) Eastman Kodak Fellow, 1956-1957.

(3) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

(4) G. J. Hoijtink, E. de Boer, P. H. van der Meij and W. P. Weyland, *Rec. trav. chim.*, **74**, 277 (1955); **75**, 487 (1956).

(5) P. Balk, G. J. Hoijtink and J. W. H. Scheurs, *ibid.*, **76**, 813 (1957).

(6) D. E. Paul, D. Lipkin and S. I. Weissman, *THIS JOURNAL*, **78**, 116 (1956).

(7) D. E. Paul, Ph.D. Thesis, Washington University, 1954.

interpretation of this spectrum is complicated by the expected double degeneracy of the electronic ground state of hexagonal benzene negative ion. The Jahn-Teller theorem⁹ indicates that the hexagonal nuclear configuration (D_{6h}) is generally not stable in the presence of orbital degeneracy. The consequences of the Jahn-Teller theorem for benzene positive ion have been investigated by Liehr,¹⁰ and more generally for hexagonal structures by Moffitt and Liehr,¹¹ and for doubly degenerate systems by Longuet-Higgins, *et al.*¹² The above mentioned investigations demonstrate that the Jahn-Teller phenomenon may lead to complex motions. Only in the limit of large distortions and heavy nuclei could benzene negative ion be properly described as a stable distorted hexagon. Since our observations indicate hexagonal symmetry, we must say that each deviation from hexagonal symmetry is of shorter duration than the characteristic time ($\sim 10^{-7}$ seconds) of the observed hyperfine interactions. Alternatively, the situation may be described by the statement that the structure averaged over a time of the order of the hyperfine period is accurately hexagonal. We are at present unable to assess the contributions to the averaging of temperature dependent activation processes and of temperature independent tunneling processes.

Analysis of the Toluene Anion Spectrum.—The e.s.r. spectrum of toluene anion consists of five equally spaced lines with interval 5.1 oersteds and intensity ratios 1:4:6:4:1. These intensity ratios are to be expected from the interaction of four equivalent protons with the unpaired electron. Although there are no four protons equivalent by symmetry in toluene negative ion, there are two possibilities for accidental equivalence: (1) the three methyl protons plus the *para*-proton and (2) the two *ortho*-protons plus the two *meta*-protons. In order to distinguish between these two possibilities *m*- and *p*-deuterotoluene anions were prepared. The *m*-deutero compound gave a four line spectrum while the *p*-deutero gave a five line spectrum indistinguishable from that of undeuterated toluene negative ion. The four line spectrum corresponds to the case of the deuteron replacing a proton which does interact with the unpaired electron. The hyperfine structure from the deuteron is too small to be resolved. The five line spectrum corresponds to the deuteron replacing a proton which does not interact. Thus the five lines spectrum of toluene negative ion must arise from the interaction of the *o*- and *m*-proton magnetic moments with the moment of the unpaired electron.

E.S.R. Spectra of the Xylene Negative Ions.—The study of the e.s.r. spectra of the xylene anions leads us to some conclusions about the nature of hyperconjugation. Both the *o*- and *p*-xylene anions give five line spectra very similar to that of the toluene anion. These spectra arise from the interaction between the four ring protons and the un-

paired electron, the methyl protons not contributing to the hyperfine pattern in either case. The spectrum of *m*-xylene anion, on the other hand, is more complex. This spectrum clearly consists of five approximately equally spaced groups of lines, each group containing at least seven components. The number of lines cannot be explained by considering the ring protons alone. The methyl protons contribute appreciable hyperfine splitting in this case.

The observed hyperfine interactions arise from non-vanishing electronic spin density at the positions of the protons.¹³ For the aromatic protons the necessary spin density is a consequence of σ - π interaction, the density at such proton being approximately proportional to the integrated density on the neighboring carbon.¹⁴⁻¹⁶ Hence the anions of toluene and *p*-xylene may be described as containing an unpaired electron in an orbital antisymmetric with respect to the reflection plane perpendicular to the ring. Wave functions of proper form may be constructed for toluene and *p*-xylene anions. For *o*-xylene, however, we have been unable to construct a single configuration function which yields the observed equality of splitting by the four ring protons. Neither treatment of the methyl groups as perturbing agents of the π -ring system nor inclusion of them as part of the conjugated system has been successful for *o*-xylene anion. Regardless of the approximation, hyperfine splitting from the methyl protons indicates that some unpairedness resides on these protons. From the MO point of view these splittings determine the amplitude of methyl hydrogen 1s functions to be included in the singly occupied orbital. If the magnitude of this amplitude measures the amount of hyperconjugation of the methyl group with the π -system, then we say that there is more hyperconjugation in *m*-xylene anion than in any of the other methyl substituted benzene anions studied. Methyl proton splittings range from less than 0.5 oersted in the *o*- and *p*-xylene anions to 7.4 oersteds in Wurster's blue.¹⁷ This indicates that hyperconjugation depends strongly on the environment of a methyl group. Even slight changes of environment as between *m*- and *p*-xylene anions makes an appreciable difference. On the other hand, indications from methyl proton splittings in substituted semiquinones are that hyperconjugation is insensitive to environmental changes of methyl groups.¹⁸ No satisfactory explanation has as yet been found to account for these variations in methyl proton splittings. A successful explanation will undoubtedly lead to a better understanding of hyperconjugation and of group-ring interactions in general.

Optical Spectra.—The optical absorption spectra of benzene and toluene anions have been studied in the range 350 to 800 $m\mu$. Only one well defined absorption maximum occurs in each case at about 675 $m\mu$.

(9) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A164**, 117 (1937).

(10) A. Liehr, *Z. physik. Chem.*, **9**, 338 (1956).

(11) M. Moffitt and A. Liehr, *Phys. Rev.*, **106**, 1195 (1957).

(12) H. C. Longuet-Higgins, U. Opiks, M. H. L. Pryce and R. A. Sack, *Proc. Roy. Soc. (London)*, **244A**, 1 (1958).

(13) S. I. Weissman, *J. Chem. Phys.*, **22**, 1378 (1954).

(14) H. McConnell and D. Chestnut, *ibid.*, **28**, 107 (1958).

(15) H. McConnell, *ibid.*, **28**, 1188 (1958).

(16) E. de Boer, *ibid.*, **25**, 190 (1956).

(17) S. I. Weissman, *ibid.*, **22**, 1135 (1954).

(18) B. Venkataraman and G. Fraenkel, *ibid.*, **23**, 588 (1955).

Exchange Rates.—Because of the fact that only a small fraction of each of the hydrocarbons is converted to the anion, the e.s.r. spectra of the anions were necessarily observed in the presence of excess hydrocarbon. For the systems naphthalene negative ion-naphthalene¹⁹ and anthracene negative ion-anthracene²⁰ rapid oxidation reduction ex-

(19) R. L. Ward and S. I. Weissman, *THIS JOURNAL*, **79**, 2086 (1957).

(20) E. de Boer, unpublished observation.

change reactions which conceal the hyperfine splittings occur. Since for the ions here described well resolved hyperfine structure was observed in the presence of neutral hydrocarbons at about 1 *M* the exchange rates are considerably lower than for the naphthalene and anthracene systems. At temperatures in the range -50 to -80° the second-order rate constants for oxidation reduction exchange are less than 5×10^5 l. mole⁻¹ sec.⁻¹.

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The Lower Hydrides of Phosphorus. III. The Interaction of Biphosphine and Diborane¹

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Diborane and boron trifluoride react with biphosphine to produce the compounds $P_2H_4 \cdot B_2H_6$ and $P_2H_4 \cdot 2BF_3$, respectively. The compound formed with diborane is more stable than biphosphine toward decomposition, with the elimination of phosphine, but the compound with boron trifluoride eliminates phosphine at temperatures above -118° . When biphosphine is treated with diborane at room temperature, both phosphine and hydrogen are evolved leading to defective solids containing boron, phosphorus and hydrogen.

Previous communications have been concerned with the decomposition of biphosphine *in vacuo* at room temperature^{2a} and in liquid ammonia at its boiling point.^{2b} In both cases phosphine is eliminated and solid hydrides of indefinite composition are produced.

In the present study we have examined the interaction of biphosphine with the Lewis acids, boron trifluoride and diborane. The compounds $P_2H_4 \cdot 2BF_3$ and $P_2H_4 \cdot B_2H_6$ are formed, respectively. The compound formed with boron trifluoride is considerably less stable than biphosphine itself and decomposes rapidly at -78° to yield both boron trifluoride and phosphine. The compound with diborane, on the other hand, is more stable than biphosphine. It may be formed at -35° where biphosphine decomposes at a measurable rate. Apparently it may also be formed at room temperature under pressure of excess diborane. Removal of excess diborane then causes the elimination of diborane, phosphine and hydrogen, leaving a defective solid containing boron, phosphorus and hydrogen. When the compound is heated rapidly to 0° dissociation and decomposition occur together.

The greater stability of $P_2H_4 \cdot B_2H_6$ as compared with $P_2H_4 \cdot 2BF_3$, or P_2H_4 itself, may be attributed to the availability of electrons in the B-H linkage to back-bond to available d-orbitals in phosphorus. An interaction of this kind would tend to augment the sigma dative bonding³ and probably increase the electron density of the P-P bond, leading to increased stability. An opposite effect might be expected here with boron trifluoride. The electro-

negative fluorine atoms probably would permit only sigma dative bonding, thus rendering the phosphorus atoms more positive and reducing the electron density of the P-P bond.

The greater chemical stability of $B_2H_6 \cdot P_2H_4$ as compared with P_2H_4 is demonstrated further by its behavior toward HCl. Thus HCl has been shown to effect a rapid decomposition of P_2H_4 into PH_3 and a yellow solid hydride at temperatures as low as -125° ,⁴ whereas HCl does not react with $P_2H_4 \cdot B_2H_6$ at a measurable rate at -78° .

Experimental

1. Reagents and Procedure.—Diborane was prepared by allowing a slurry of lithium aluminum hydride in anhydrous di-*n*-butyl ether to react with the di-*n*-butyl etherate of boron trifluoride. The diborane as produced was swept from the reaction vessel with nitrogen through two traps cooled to -78 and -119° , respectively. It was collected in a trap covered with liquid air then transferred to a two liter storage vessel equipped with a Stock valve and a manometer. Biphosphine was prepared and purified as described previously.¹

Reactants were measured out by volume as gases in a calibrated section of the vacuum apparatus. Condensable products were separated by fractional condensation and characterized by standard methods. The analyses of mixtures of diborane and phosphine were carried out by hydrolyzing the diborane and measuring the hydrogen formed in the hydrolysis, along with residual phosphine. Results on mixtures were checked by molecular weight determinations.

2. Reaction of Biphosphine and Diborane at Low Temperature.—A measured excess of diborane was added to a given amount of biphosphine. The course of the reaction was followed by measuring the unreacted diborane. The latter was removed at -78° where the vapor pressure of biphosphine is less than one mm.¹ Although biphosphine melts at -92° ,³ reaction with diborane occurs below this temperature. The reactions were allowed to continue at the temperatures indicated in Table I until it was established that the consumption of diborane was negligible over a 24 hr. period. The final molar ratios show that $P_2H_4 \cdot B_2H_6$ was formed. This is a white solid, stable at -78° and possessing no appreciable vapor pressure.

(1) Presented before the Inorganic Division, American Chemical Society, 132nd National Meeting, New York City, September, 1957.

(2) (a) E. C. Evers and E. H. Street, Jr., *THIS JOURNAL*, **78**, 5726 (1956); (b) E. H. Street, Jr., D. M. Gardner and E. C. Evers, *ibid.*, **80**, 1819 (1958).

(3) W. A. G. Graham and F. G. A. Stone, *Chem. Ind.*, 319 (1956).

(4) R. Royen and K. Hill, *Z. anorg. allgem. Chem.*, **229**, 97 (1936)