

line that correlates the experimental points for the acyl hydroperoxides and the more acidic alkyl hydroperoxides has a slope (β_{lg}) equal to -0.63 , whereas the less acidic alkyl hydroperoxides form a separate series correlated by a best line of slope (β_{lg}) equal to -0.18 . A similar behavior is seen for the linear free energy relationship at pH 6.77. In this case, β_{lg} for the acyl hydroperoxides and more acidic alkyl hydroperoxides is -0.36 and the corresponding β_{lg} value for the less acidic alkyl hydroperoxides is -0.11 . These observations show that there is a break in the linear free energy plots. From a previous study in methanol the value of β_{lg} obtained for the reaction of (TPP)Fe^{III}(Cl) with acyl hydroperoxides and the more acidic alkyl hydroperoxides is -0.36 ,

whereas with less acidic alkyl hydroperoxides the value of β_{lg} is -0.15 .^{1a,c} The agreement in the values of β_{lg} for the reaction of acyl hydroperoxides and more acidic alkyl hydroperoxides with (TPP)Fe^{III}(Cl) in methanol solvent and with (1)Fe^{III}(H₂O)(X) in H₂O at pH 6.77 (-0.36 vs -0.36) and the similarity in β_{lg} for the less acidic alkyl hydroperoxides (-0.11 vs -0.15) establish that our observations in methanol, in which the pH of the medium could not be accurately maintained, are valid.

Acknowledgment. This work was supported by funds from the National Institutes of Health and the National Science Foundation.

Communications to the Editor

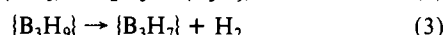
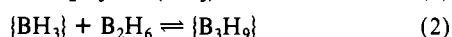
Identity of the Rate-Determining Step in the Gas-Phase Thermolysis of Diborane: A Reinvestigation of the Deuterium Kinetic Isotope Effect

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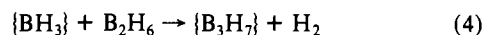
Received May 22, 1989

The gas-phase thermolysis of diborane is known to be homogeneous in its initial stages and to follow $3/2$ -order kinetics over a wide range of temperature and pressure.¹⁻³ This suggests that a triborane species is involved in the rate-determining step, and the currently favored mechanism involves a three-step process:³⁻⁵



A triborane species has been generated by reaction of $\{\text{BH}_3\}$ with B_2H_6 in a fast-flow system and detected mass spectrometrically, but it was not possible to determine the number of hydrogen atoms in the species.⁶

Cogent arguments have been advanced to suggest that step 3 is the rate-determining step,^{3,4} but a very recent high-level computational study employing many-body perturbation theory and the coupled-cluster approximation implies that it is the formation of $\{\text{B}_3\text{H}_9\}$ (step 2) rather than its decomposition (step 3) that is rate-determining.⁷ The calculations also indicate that the $\{\text{B}_3\text{H}_9\}$ formed in step 2 carries about 80 kJ mol⁻¹ of excess internal energy, suggesting that step 3 might occur so rapidly that for all practical purposes the formation of $\{\text{B}_3\text{H}_7\}$ might best be represented by the direct reaction:



This possibility, which had been considered earlier but tentatively dismissed,³ is easier to reconcile with the qualitative observation that added H₂ not only inhibits the rate of decomposition of B_2H_6 ¹ but also alters the product distribution in favor of volatile boranes;⁸

our own quantitative studies with Dr. M. D. Attwood^{5,9} show that the initial rate of decomposition of B_2H_6 at 3.5 mmHg and 150 °C is decreased by a factor of 3.4 in the presence of a 14-fold excess of H₂.

The computations⁷ also addressed the question of the relative rates of decomposition of B_2H_6 and B_2D_6 and found that, at 127 °C, the ratio of the rate constants ($k_{\text{H}}/k_{\text{D}}$) was 1.73 if step 2 were rate-determining and 2.4 if the rate-determining step were step 3; unfortunately the only experimental determination of this ratio (which was based on the relative rates of production of H₂ and D₂ at 88 °C)³ gave a value of 5.0, which is compatible with neither of the computed values.

In an attempt to resolve these difficulties, we decided to undertake a careful experimental reinvestigation of the relative rates of decomposition of B_2H_6 and B_2D_6 using a mass spectrometric technique to monitor the initial stages of the reaction. We chose to monitor the rate of consumption of diborane rather than the rate of production of hydrogen since this was a more direct measure to compare with the calculated rates. The reactions were carried out at 147 °C in preconditioned spherical Pyrex bulbs (volume ca. 1 dm³) with initial pressures of diborane about 3.5 mmHg; helium, argon, and krypton at partial pressures of 100, 1.0, and 1.0 mmHg, respectively, were also present as calibrants, etc., as previously described.^{10,11} Initial rates were obtained by the tangent method from plots of diborane pressure vs time for 14 separate runs with B_2H_6 and 10 runs with B_2D_6 ; these yielded values for the $3/2$ -order rate constants $k_{\text{H}} = (4.55 \pm 0.89) \times 10^{-4}$ and $k_{\text{D}} = (1.77 \pm 0.28) \times 10^{-4}$ mol^{-1/2} m^{3/2} s⁻¹, respectively. The value of the ratio $k_{\text{H}}/k_{\text{D}}$ is therefore 2.57 ± 0.65 , which is clearly more consistent with the computed values⁷ than with the early experimental value based on the rates of production of H₂ and D₂.³ The new experimental value is closer to the computed value of 2.4 assuming step 3 as rate-determining than to the value of 1.73 for step 2 as rate-limiting, but in view of the expected uncertainties in the theoretical values, it is probably more appropriate to suggest that both of the computed values are in adequate agreement with the new experimental value.¹² We note parenthetically that the computed overall activation energy for the decomposition of diborane is 134 kJ mol⁻¹ if step 2 is rate-determining but only 92 kJ mol⁻¹ if step 3 is rate-determining;⁷ our own most recent experimental redetermination of this quantity

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(based on the rate of consumption of B_2H_6 at 11 temperatures in the range 120–180 °C) is $102.6 \pm 3.3 \text{ kJ mol}^{-1}$. Again it would be unwise to place too great a significance on these differences, and it is probable that calculations with a larger basis set or incorporating the possibility of tunneling would lead to a revision of the computed values for the activation energy.^{7,12}

In summary, a careful reinvestigation of the relative initial rates of decomposition of B_2H_6 and B_2D_6 has led to a value of 2.57 ± 0.65 for the rate-constant ratio k_H/k_D , which disagrees with an earlier experimental value but is close to values obtained in a recent high-level computational study. This important new result therefore removes a potential inconsistency between experiment and computation. Taken in conjunction with the experimentally observed influence of added H_2 in repressing the rate of decomposition of B_2H_6 and in altering the distribution of products, the totality of experimental and computational evidence suggests that the rate-determining step following the symmetric dissociation of diborane is neither simply the formation of $\{B_3H_9\}$ from $\{BH_3\}$ and B_2H_6 nor the subsequent decomposition of $\{B_3H_9\}$ to give $\{B_3H_7\}$ and H_2 , but the concerted formation and decomposition of $\{B_3H_9\}$ as represented by step 4.

Acknowledgment. We thank Professors J. F. Stanton and W. N. Lipscomb for sending us a preprint of their paper, D. Singh for assistance with the mass spectrometers, and SERC for a maintenance grant (to S.M.L.), and the U.S. Army Research and Standardization Group (Europe) for financial support.

Registry No. B_2H_6 , 19287-45-7; B_2D_6 , 20396-66-1.

Direct Observation of η^2 -Arene Complexes of $[(C_5Me_5)Rh(PMe_3)]$

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Received June 13, 1989

Over the past few years, there has been substantial progress in studies of the mechanism of activation of aliphatic and aromatic C–H bonds by transition metals.¹ In particular, earlier studies in our group have indicated that arenes coordinate to $[(C_5Me_5)Rh(PMe_3)]$ in an η^2 fashion prior to C–H bond oxidative addition, and that this initial coordination permits the activation of aromatic C–H bonds to compete with aliphatic C–H bond activation.² The evidence for η^2 -arene coordination relies heavily on indirect experiments (intramolecular isomerization of an aryl deuteride,² kinetic isotope effect experiments³), as the only direct evidence for arene coordination was with *p*-di-*tert*-butylbenzene at low temperature.⁴ We report here the room temperature observation of η^2 -arene complexes of $[(C_5Me_5)Rh(PMe_3)]$ and an equilibrium between an η^2 -arene complex and its aryl hydride counterpart.

The aryl hydride complex $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**) is well established to lose benzene upon heating to 60 °C. In the presence of an excess of another arene, a new aryl hydride complex is formed in high yield. However, when the complex is heated in hexane solution containing 10 equiv of phenanthrene, a single new product is formed for which no hydride resonance is observed by ¹H NMR spectroscopy. Furthermore, the ³¹P doublet resonance of the starting material at δ 7.90 ($J_{P-Rh} = 156 \text{ Hz}$) is replaced

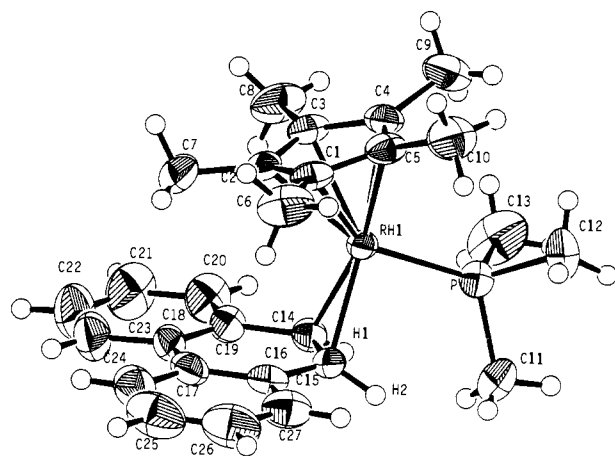
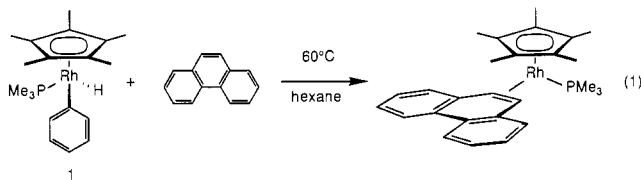


Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$; ellipsoids shown at the 50% level. Important distances (Å) and angles (deg): Rh–C14, 2.128 (4); Rh–C15, 2.144 (4); C14–C15, 1.428 (6); C14–C19, 1.469 (5); C15–C16, 1.460 (5).

by a new doublet at δ 0.31 ($J_{P-Rh} = 201 \text{ Hz}$). The upfield shift and increase in coupling constant are typical of the spectral changes characteristic of a change from Rh(III) to Rh(I) in a variety of $CpRhL_n$ and $(C_5Me_5)RhL_n$ complexes.⁵ The multiplicity of the ¹H NMR spectrum of the arene ligand (four multiplets in the aromatic region and a multiplet at δ 3.56)⁶ suggests the symmetrical coordination of the central double bond to the metal center as shown in eq 1.



A single-crystal X-ray structure of this material confirms the above formulation as an η^2 -arene complex as shown in Figure 1.⁷ The central olefinic double bond of phenanthrene is slightly lengthened compared to free phenanthrene, and the rhodium center lies at a slightly obtuse angle to the planar arene ring. The fused ring system is oriented away from the phosphine ligand, as the other rotamer would superimpose the rings upon the phosphine.

Several other η^2 -arene complexes have been structurally characterized, including $[P(Cy)_3]_2Ni(\eta^2\text{-anthracene})$,⁸ $(PEt_3)_2Pt[\eta^2-C_6(CF_3)_6]$,⁹ $[CpRe(CO)_2]_2(\mu\text{-}\eta^2\text{-}C_6H_6)$,¹⁰ $CpRh(PMe_3)(\eta^2\text{-}C_6F_6)$,¹¹ and a variety of Ag^+ (arene)¹² complexes. In

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(6) For $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$ ¹H NMR ($c\text{-}C_6D_{12}$): δ 1.083 (d, $J = 2.5 \text{ Hz}$, 15 H), 1.151 (d, $J = 8.2 \text{ Hz}$, 9 H), 3.560 (dd, $J = 8.0, 2.5 \text{ Hz}$, 2 H), 6.981 (t, $J = 7.6 \text{ Hz}$, 2 H), 7.118 (t, $J = 7.4 \text{ Hz}$, 2 H), 7.265 (d, $J = 8.1 \text{ Hz}$, 2 H), 7.946 (d, $J = 8.0 \text{ Hz}$, 2 H). Anal. Calcd (found) for $RhPC_{27}H_{34}$: C, 65.85 (65.53); H, 6.96 (7.03).

(7) $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$ crystallizes in monoclinic space group $P2_1/c$ with $Z = 4$, $a = 9.922$ (4) Å, $b = 16.004$ (6) Å, $c = 15.29$ (1) Å, $\beta = 82.12$ (5)°. Standard Patterson map solution of the structure and full least-squares refinement of the 2421 data $>3\sigma$ converged with $R_1 = 0.025$, $R_w = 0.036$.

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