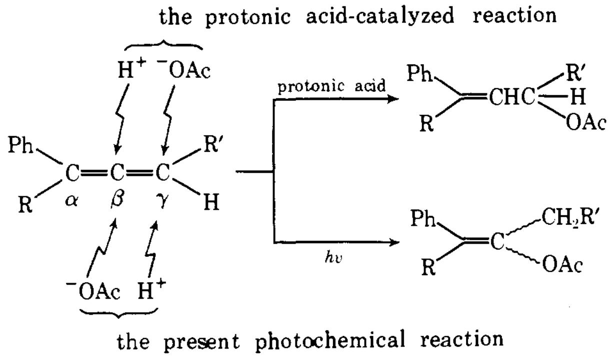
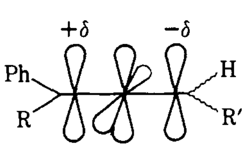
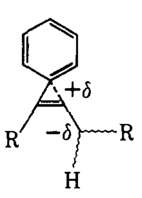
Scheme I



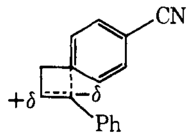
Species **4** is similar to that investigated theoretically as a lowest excited state structure of an allene.[7] The tentative structure **5** conceptually resembles the zwitterionic species **6** which was suggested in the anti-Markownikoff photochemical addition of methanol to 3-(*p*-cyanophenyl)-1-phenylpropene[1o,p] and resembles the vinylidene phenonium ion which was investigated in the solvolyses of 3-phenyl-2-buten-2-yl triflates.[8]



4



5



6

Thus, the photochemical polar additions of acetic acid to the phenylallenes possess two characteristic aspects. (1) The regioselectivity observed in the photochemical reactions of phenylallenes is quite different from that of the nonphotochemical protonic acid-catalyzed reactions. (2) These photochemical reactions seem to proceed mainly through the triplet excited state even though the structure of the allene is acyclic.

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(2) An anti-Markownikoff addition was reported in the photochemical reaction of 3-(*p*-cyanophenyl)-1-phenylpropene with methanol. See literature 1o and 1p.

(3) All of the products were characterized by NMR, ir, and mass spectra and identified with the corresponding authentic specimens prepared independently.

(4) $\epsilon_{254}$ was estimated to be 50 for *trans*-1,3-pentadiene and 20 for *cis*-1,3-pentadiene in a polar solvent (S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973, p 5) while $\epsilon_{254}$ of **1c** was 1.3 × $10^4$ in methanol or 1.4 × $10^4$ in *n*-hexane. Under the condition of this quenching experiment, the quencher absorbs at most 1% of the light (254 nm). Therefore the observed quenching of the reaction of **1c** cannot be accounted for by the absorption of the quencher. The preliminary Stern–Volmer plot ($\Phi_0/\Phi_{\text{quencher}}$ vs. [quencher]) showed a typical pattern suggesting that two excited states are involved in the addition.

(5) The absorbances of **1a** and **1b** at 254 nm are very weak. $\epsilon_{254}$ of **1a:** 15 (MeOH), 10 (*n*-hexane). $\epsilon_{254}$ of **1b:** 8 (MeOH), 4 (*n*-hexane). The difference of reactivity between **1a–b** and **1c–e** seems to be attributable to the difference in absorption.

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**Kahee Fujita,* Kazumasa Matsui, Tatsuya Shono**
*Department of Synthetic Chemistry, Kyoto University*
*Kyoto, Japan*

*Received April 23, 1975*

## Acid Dissociation of Chloroform and Phenylacetylene. Solvent Isotope Effects[1]

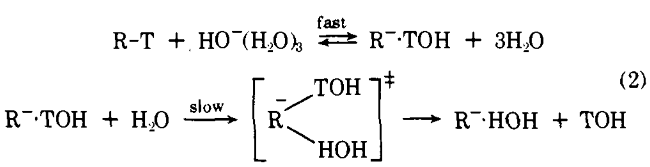
*Sir:*

Kinetic isotope effects are frequently used to gauge transition state structure, and in particular to estimate the extent of proton transfer at transition states of proton transfer reactions. Use of the solvent isotope effect on proton transfer to the aqueous hydroxide ion, eq 1,

$$\mathrm{SH + HO^-(H_2O)_3 \longrightarrow S^- + 4H_2O}$$

in this way, however, is complicated by the possibility that one of the three water molecules in the primary solvation shell of this ion, which is where most of the isotope effect resides, must be completely removed before proton transfer can begin. However, this complication will play a decreasingly important role as the degree of proton transfer increases, and it should vanish entirely when proton transfer becomes complete, i.e., reactions in which proton transfer is finished by the time the rate-determining transition state is reached should give a full or equilibrium value of this isotope effect.

It is curious, therefore, that the detritiation of phenylacetylene, a seemingly uncomplicated example of this reaction type, has been reported to give an effect which falls considerably short of the expected limiting value. In this reaction, hydrogen ion transfer is believed to be rapid and reversible while subsequent exchange of the transferred hydrogen with the solvent pool is slow (eq 2);[2] proton transfer



$$\mathrm{R{-}T + HO^-(H_2O)_3 \overset{fast}{\rightleftharpoons} R^-{\cdot}TOH + 3H_2O}$$
$$\mathrm{R^-{\cdot}TOH + H_2O \xrightarrow{slow} \left[\overset{-}{R}\begin{matrix}\diagup TOH\\ \diagdown HOH\end{matrix}\right]^{\ddagger} \longrightarrow R^-{\cdot}HOH + TOH} \qquad (2)$$

is therefore complete at the rate-determining transition state.[3] In an early study of this reaction,[4] $k_{\mathrm{D_2O}}/k_{\mathrm{H_2O}}$ was found to be 1.60,[5] and yet a limiting value half again as large, $k_{\mathrm{D_2O}}/k_{\mathrm{H_2O}} = 2.4$, can be reliably estimated from the measured effect on the autoprotolysis of water and the known fractionation factor of the hydronium ion.[6]

We wish to report that we have corroborated this unexpected behavior and that we have also done further experiments which provide an explanation for the apparent anomaly. We find $k_{\mathrm{D_2O}}/k_{\mathrm{H_2O}} = 1.36$ for the detritiation of phenylacetylene and also $k_{\mathrm{D_2O}}/k_{\mathrm{H_2O}} = 1.48$ for the experimentally more accessible detritiation of chloroform, another reaction thought to occur by the same mechanism (eq 2).[7] This value for chloroform is listed in Table I together with three other isotope effects we have measured for the hydrogen exchange of this substance catalyzed by hydroxide ion. In these other experiments (systems II–IV), tritium was

Table I. Isotope Effects on Hydrogen Exchange in Chloroform in Aqueous Solution at 25°

| System[a] | $k_D/k_H$ Obsd | $k_D/k_H$ Theor |
|---|---|---|
| I. $RT \xrightarrow[L_2O]{LO^-} RL$ | 1.48 ± 0.02 | $\phi^{\ddagger}/\phi_h$ |
| II. $RL \xrightarrow[L_2O]{LO^-} RT$ | 2.10 ± 0.10 | $\phi^{\ddagger}/\phi_s\phi_h$ |
| III. $RH \xrightarrow[L_2O]{LO^-} RT$ | 2.28 ± 0.03 | $1/\phi_h$ |
| IV. $RL \xrightarrow[H_2O]{HO^-} RT$ | 0.97 ± 0.04 | $\phi^{\ddagger}/\phi_s$ |

[a] The symbol "L" is used to designate the hydrogens which are changed from H to D in the comparison, i.e., L = H or D.

present initially, in tracer amounts, in the solvent only, and rates of tritium incorporation rather than detritiation were determined; initial rate measurements were made where necessary in order not to alter the isotopic identity of the substrate.

These data lend themselves particularly well to analysis by the fractionation factor method. By this technique, solvent isotope effects become simple ratios of fractionation factors: those for all isotopically exchanged sites of the transition state divided by corresponding factors for the initial state. Thus, for system I, $k_{D_2O}/k_{H_2O} = \phi^{\ddagger}/\phi_h$, where $\phi^{\ddagger}$ is the D-H fractionation factor, relative to the solvent, for the incoming hydrogen of the transition state (see eq 2), and $\phi_h$ is the factor for the aqueous hydroxide ion in the initial state ($\phi_h$ is a composite factor which includes the hydrogen of this ion as well as those of its solvating water molecules). Similar expressions may be written for the other three systems; these are listed in Table I. The additional symbol $\phi_s$ is the fractionation factor for the exchanging hydrogen in the substrate.

These relationships and the corresponding experimental values of the isotope effects form a set with fewer unknowns ($\phi^{\ddagger}$, $\phi_h$, and $\phi_s$) than pieces of data. The model can therefore be tested for internal consistency. For example, the fractionation factor ratio for system II is equal to the product of those for systems III and IV, and it is significant therefore that $(k_{D_2O}/k_{H_2O})_{III} \times (k_{D_2O}/k_{H_2O})_{IV} = (2.28 \pm 0.03) \times (0.97 \pm 0.04) = 2.21 \pm 0.09$, in good agreement with $(k_{D_2O}/k_{H_2O})_{II} = 2.10 \pm 0.10$.

Solution of this system of equations gives $\phi^{\ddagger} = 0.65 \pm 0.01$, $\phi_h = 0.44 \pm 0.01$, and $\phi_s = 0.68 \pm 0.02$. The fact that $\phi^{\ddagger}$ is appreciably less than unity shows that there is appreciable isotopic fractionation in the incoming (or outgoing) water molecule of the rate-determining transition state (eq 2). This is a reasonable result, inasmuch as this molecule is in the process of forming a hydrogen bond to a localized carbanion; in this respect, it is similar to the water molecules which form the primary hydration shell of the hydroxide ion, and these are known to be subject to considerable isotopic fractionation.

As the fractionation factor expression for system I shows, the effect of $\phi^{\ddagger}$ is to offset $\phi_h$ and thereby to make the solvent isotope effect on detritiation smaller than the expected limiting value. It is only when *both* outgoing and incoming hydrogens remain unchanged, as in system III, that the full effect of $\phi_h$ can be felt, and it is gratifying therefore that the isotope effect found for system III, $k_{D_2O}/k_{H_2O} = 2.28 \pm 0.03$, is in reasonably good agreement with the limiting or equilibrium value of 2.4.

**Acknowledgment.** We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support of this work.

## References and Notes

(1) This research was performed at the Illinois Institute of Technology and forms part of a thesis submitted there by A. C. Lin in partial fulfillment of the requirements for the Ph.D. degree.

(2) Exchange is shown here as occurring via complete replacement of the original solvating water molecule generated by neutralization of the hydroxide ion. It could also be effected by a simple rotation of this water molecule which brings its other hydrogen into covalent bond-forming position, but the analysis of isotope effects using that mechanism would be no different from that presented here. The same is true of mechanisms in which the incoming and outgoing hydrogens are not equivalent.

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(5) The value actually reported is 1.34. That, however, was calculated using isotope effects on the acid dissociation of biphosphate ion and the autoprotolysis of water which have since been superseded; when modern values are used, the result increases to 1.60.

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**A. J. Kresge***
*Scarborough College, University of Toronto*
*West Hill, Ontario M1C 1A4, Canada*

**A. C. Lin**
*Department of Chemistry, University of Rochester*
*Rochester, New York 14627*

*Received April 1, 1975*

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## Halogenated Octahydroborate Salts. A New Route to Pentaborane(9)

*Sir:*

We wish to report the first preparation of halogen-substituted triborohydride salts and their use in a new and extremely convenient synthesis of pentaborane(9). The synthesis allows scale-up with simple equipment and provides a product from readily prepared starting materials in respectable yield and free of the bothersome pentaborane(11) contamination encountered with other methods.[1,2]

Tetrabutylammonium octahydroborate(−1), mp 217–218° was obtained from the oxidation of borohydride ion with iodine at 100°.[3] A 0.1561-g sample of the salt (0.552 mmol) dissolved in 0.8940 g of dry $CH_2Cl_2$ in an evacuated tube produced a vapor pressure depression of 39 mmHg relative to pure solvent (353 mm at 20°), with a vapor volume of 310 ml. When bromine-free HBr gas (0.551 mmol) was condensed onto the sample, hydrogen gas was evolved rapidly on warming (0.557 mmol). Complete evaporation of the solvent left a solid residue and a weight gain of 0.0412 g, compared to a gain of 0.0418 g calculated on the basis of the equation

$$(C_4H_9)_4NB_3H_8 + HBr \rightarrow (C_4H_9)_4NB_3H_7Br + H_2$$

Return of the solvent now gave a vapor pressure depression of 37 mm. On the assumption that $(C_4H_9)_4NB_3H_8$ and the product have the same Van't Hoff factor, these data correspond to a formula weight of 368 for the product, in good agreement with the value of 361 calculated for $(C_4H_9)_4NB_3H_7Br$. The nature of the reaction remained unchanged when diethyl ether was used as solvent. Evaporation of the solvent left a white crystalline solid which decomposed on heating. Anal. Calcd for $(C_4H_9)_4NB_3H_7Br$: C, 53.1; H, 12.0; N, 3.9; Br, 22.1. Found: C, 53.4; H, 12.1; N, 3.9; Br, 21.7.

These results were completely unexpected since it had been demonstrated that reaction of $NaB_3H_8$ with HCl gives rapidly a $B_3H_7$ intermediate,[4] and that $(NH_3)_2BH_2B_3H_8$