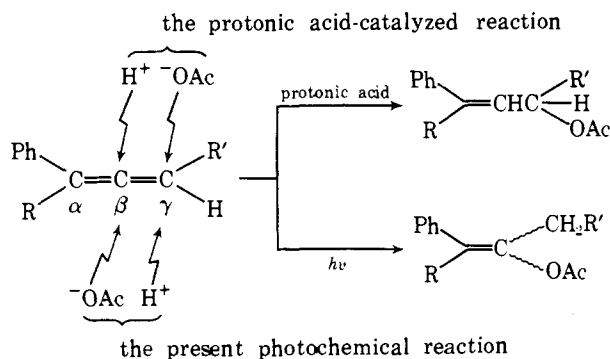
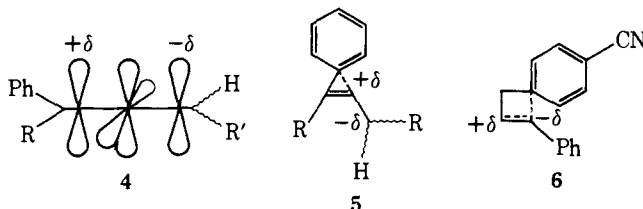


Scheme I



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^{10,p} and resembles the vinylidene phenonium ion which was investigated in the solvolyses of 3-phenyl-2-buten-2-yl triflates.⁸



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.

References and Notes

- (a) J. A. Marshall, *Acc. Chem. Res.*, **2**, 33 (1969); (b) H. Kato and M. Kawanisi, *Tetrahedron Lett.*, 895 (1970); (c) P. J. Kropp, E. J. Peardon, Jr., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., *J. Am. Chem. Soc.*, **95**, 7058 (1973); (d) B. J. Ramey and P. D. Gardner, *ibid.*, **89**, 3949 (1967); (e) P. J. Kropp, *ibid.*, **89**, 3650 (1967); (f) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967); (g) P. J. Kropp, *ibid.*, **91**, 5783 (1969); (h) *ibid.*, **88**, 4091 (1966); (i) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966); (j) J. A. Marshall and A. R. Hochstetler, *ibid.*, **91**, 648 (1969); (k) S. Fujita, T. Nomi, and H. Nozaki, *Tetrahedron Lett.*, 3557 (1969); (l) K. Fujita, K. Yamamoto, and T. Shono, *ibid.*, 3865 (1973); (m) N. Miyamoto, M. Kawanisi, and H. Nozaki, *ibid.*, 2565 (1971); (n) M. Kawanisi and K. Matsunaga, *J. Chem. Soc., Chem. Commun.*, 313 (1972); (o) S. S. Hixon, *Tetrahedron Lett.*, 4211 (1971); (p) *J. Am. Chem. Soc.*, **94**, 2505 (1971); (q) D. V. Rao, V. Lambert, and H. M. Gardner, *Tetrahedron Lett.*, 1613 (1969); (r) S. Hixon, *ibid.*, 277 (1973); (s) J. D. Roberts, L. Ardemagni, and H. Shechter, *J. Am. Chem. Soc.*, **91**, 6185 (1969); (t) J. D. Roberts, *Chem. Commun.*, 362 (1971); (u) S. F. Nelson and P. J. Hints, *J. Am. Chem. Soc.*, **91**, 6190 (1969); (v) H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, 2025 (1968); (w) T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **88**, 2602 (1966).
- An anti-Markownikoff addition was reported in the photochemical reaction of 3-(*p*-cyanophenyl)-1-phenylpropene with methanol. See literature 1o and 1p.
- All of the products were characterized by NMR, ir, and mass spectra and identified with the corresponding authentic specimens prepared independently.
- ϵ_{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 ϵ_{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.
- The absorbances of **1a** and **1b** at 254 nm are very weak. ϵ_{254} of **1a**: 15 (MeOH), 10 (*n*-hexane). ϵ_{254} of **1b**: 8 (MeOH), 4 (*n*-hexane). The differ-

ence of reactivity between **1a-b** and **1c-e** seems to be attributable to the difference in absorption.

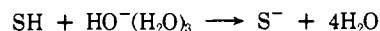
- (a) T. Okuyama, K. Izawa, and T. Fueno, *Tetrahedron Lett.*, 3295 (1970); *J. Am. Chem. Soc.*, **95**, 6749 (1973); (b) T. L. Jacobs and R. N. Johnson, *Tetrahedron Lett.*, 6397 (1960); (c) R. K. Sharma, Doctoral Thesis, University of Texas, 1964; *Diss. Abstr.*, **25**, 108 (1964); (d) A. V. Fedorova and A. A. Petrov, *J. Gen. Chem. USSR*, **31**, 3273 (1961).
- (a) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966); (b) W. T. Borden, *J. Chem. Phys.*, **45**, 2512 (1966).
- (a) P. J. Stang and T. E. Dueber, *J. Am. Chem. Soc.*, **95**, 2683 (1973); **95**, 2686 (1973).

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 Effects¹

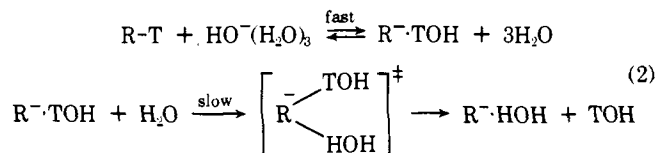
Sir:

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,



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



is therefore complete at the rate-determining transition state.³ In an early study of this reaction,⁴ $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$ was found to be 1.60,⁵ and yet a limiting value half again as large, $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.4$, 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 $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.36$ for the detritiation of phenylacetylene and also $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.48$ 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