$X = C_6H_5$) has the M − 57 ion as base peak and the *m/e* 135 and 134 ions are absent. Apparently, different types of carbon-linked substituents control fragmentation of the molecular ions, albeit paths a, b, and c are predominantly involved.

Phosphorus-Linked Substituents.—In a recent report,[18] the mass spectrum of methyl 1-adamantanephosphonate [1, $X = P(O)(OCH_3)_2$] indicates that the 1-adamantyl ion, *m/e* 135, is also the base peak.

Registry No.—1-AdmO$(CH_2)_2NH_2$·HCl, 21623-89-2; 1-AdmNHCH_3·HCl, 3717-39-3; 1-AdmNH$(CH_2)_2$-NH_2·HCl, 37819-00-4; 1-AdmCH_2NH_2·HCl, 1501-98-0.

[18] E. S. Shepeleva, P. I. Sanin, D. M. Oleinik, E. I. Bagrii, and A. A. Polyakova, *Dokl. Akad. Nauk USSR*, **203**, 608 (1972).

Kinetics of the Peracid Oxidation of Acetylenes. Electrophilic Attack on Phenylacetylenes[1]

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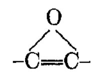
Received July 25, 1972

The peracid oxidation of phenyl- and diphenylacetylenes suggests the rate-determining primary formation of oxirenes.[2]



An oxirene intermediate was verified in the peracid oxidation of cyclodecyne,[3] the Wolff rearrangement,[4] and the reaction of methylene with carbon monoxide.[5] Earlier reports[6-8] postulated an electrophilic attack of peracid on a triple bond, but the higher reactivity of triple-bond carbon toward nucleophiles[9] might enable a nucleophilic attack of peroxide ion to occur. Contrary to the anticipation, our kinetic data on the perbenzoic acid (PBA) oxidation of phenylacetylenes showed an electrophilic attack alone as shown below and added an example of electrophilic addition to triple bond similar to the acid-catalyzed hydration.[10]

Results and Discussion

The rate of the reaction of phenylacetylene with perbenzoic acid (PBA) was measured in benzene at 25.0°. The rate was expressed as eq 1.

$$v = k[\mathrm{PhC{\equiv}CH}][\mathrm{PBA}] \qquad (1)$$

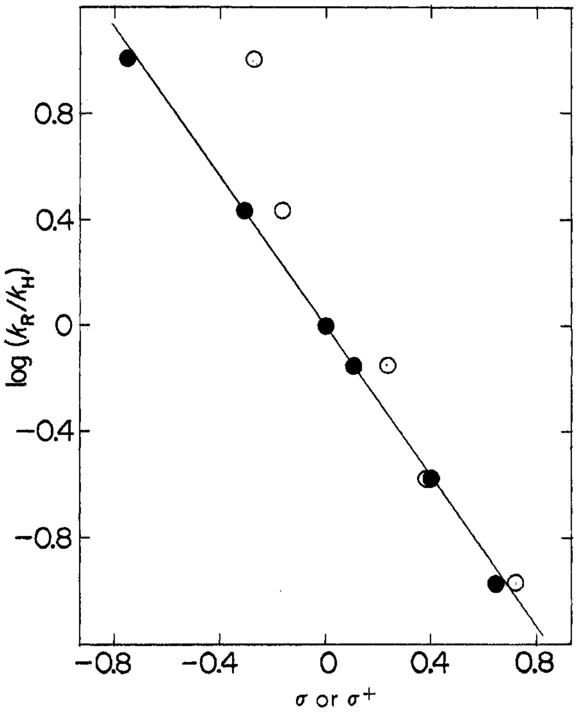


Figure 1.—Hammett plot for the reaction of substituted phenyl acetylenes with perbenzoic acid at 25.0°: open circle, σ; closed circle, σ+.

Table I

Relative Rate Constants (k_R/k_H) for the Reaction of Substituted Phenylacetylenes with Perbenzoic Acid in Benzene at 25.0° ± 0.1°[a]

Registry no.	R in $RC_6H_4C{\equiv}CH$	Relative second-order rate constant (k_R/k_H)
768-60-5	*p*-MeO	10.2[c]
766-97-2	*p*-Me	2.67[b]
536-74-3	H	1.00
873-73-4	*p*-Cl	0.680[b]
766-81-4	*m*-Br	0.263[c]
3034-94-4	*m*-NO_2	0.108[c]

[a] Initial concentrations: [$PhCO_3H$], 0.2–0.4 *M;* [$RC_6H_4C{\equiv}CH$], 0.06–0.25 *M.* [b] Probable error: ±1%. [c] Probable error: ±2%.

The second-order rate constant k ($1.65 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$) with excess phenylacetylene calculated from the pseudo-first-order rate constant agreed with that with excess PBA ($1.44 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$). This fact shows that phenylacetylene reacts with PBA in a molar ratio of *ca.* 1:1 under these conditions.[11]

Relative rates for substituted phenylacetylenes were determined by the competitive reaction as shown in Table I. The Hammett plot (Figure 1) gives a satisfactory straight line with σ+ value[12] to give a ρ value of −1.40 with a correlation coefficient r of 0.999. The negative ρ value suggests an electrophilic attack of

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[1] Contribution No. 188.

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[3] J. Ciabattoni, R. A. Campbell, C. A. Renner, and P. W. Concannon, *ibid.*, **92**, 3826 (1970).

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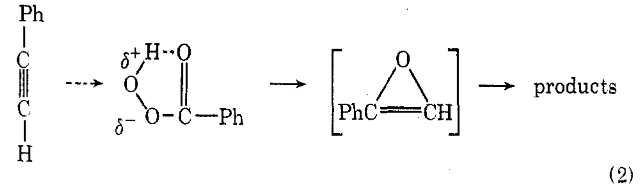
[9] E. Winterfeldt, "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 267.

[10] (a) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **90**, 1020 (1968); (b) D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *ibid.*, **87**, 2295 (1965).

[11] The pseudo-first-order rate constant from the reaction with excess PBA remains constant within the experimental error in spite of the change of the molar ratio of stoichiometry (phenylacetylene:PBA) from 1:1 to 1:2. On the other hand, the pseudo-first-order rate constant from the reaction with excess phenylacetylene should change with the change in the molar ratio of the stoichiometry. Observed approximately identical values of the two second-order rate constants from the two methods with excess PBA and excess phenylacetylene show that the molar ratio of the stoichiometry is 1:1 rather than 1:2. In view of the literature[2a] together with our identification of phenylacetic acid, phenylketene may be an initial main product of this reaction of phenylacetylene with PBA.

[12] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

peroxidic oxygen to form the oxirene ring. Since PBA in benzene forms a five-membered intramolecular hydrogen bond, the mode of attack may be as follows.



(2)

The effect of substituents on the PBA epoxidation of styrenes[13] was reported to be correlated with the Yukawa–Tsuno equation[14] [log $(k/k_0) = \rho\ (\sigma + r\Delta\sigma^{+}_{R})$] ($\rho = -1.30$ and $r = 0.48$). The ratio of the ρ value for the PBA oxidation of phenylacetylenes to that for styrenes at 25.0° was 1.08. The ρ value (*vs.* σ^+) for acid-catalyzed hydration of phenylacetylenes[10] (−3.84) and that of styrenes[15] (−3.42) give a ratio of 1.12, which is close to the above ratio for the peracid oxidation. Hence, the attacks of peroxidic oxygen on triple and double bonds possess a polar effect analogous to that observed in protonation.

The r value in the Yukawa–Tsuno equation for our reaction is 1.0, which is larger than the r value of 0.48 for styrenes. The higher r value, *i.e.*, larger contribution of resonance for phenylacetylenes, shows that less (*ca.* $^1/_{60}$) reactive phenylacetylenes have a transition state stabilized more by conjugation between the reaction site and the phenyl group. One of the p orbitals of the triple bond, which is coplanar with the benzene ring, seems to participate in the reaction in the transition state. When its p-orbital electrons attack peroxidic oxygen, the positive charge generated on the reaction site is stabilized by delocalization to p orbitals of the benzene ring.

The solvent effect is shown in Table II. Addition of ethanol, a more basic solvent, to the nonpolar solvent benzene markedly decreases the rate. The peracid forms an intramolecular hydrogen bond in benzene.[16] The intramolecular bond changes to the intermolecular one by addition of more basic ethanol resulting in a decrease of rate. Strangely, the rate in aqueous ethanol is higher than that in benzene–ethanol. This suggests that the oxidation rate *via* an intermolecular hydrogen bonded peracid is increased by increasing solvent polarity as well as by decreasing solvent basicity. In fact, the same result has been obtained in the epoxidation of styrene.[17]

TABLE II

SOLVENT EFFECT ON THE SECOND-ORDER RATE CONSTANTS (k) FOR THE REACTION OF PHENYL- AND *p*-METHYLPHENYLACETYLENES WITH PERBENZOIC ACID AT 25.0 ± 0.1°

Solvent (v/v)	$C_6H_5C{\equiv}CH$, $10^5\,k$, M^{-1} sec^{-1}	*p*-$MeC_6H_4C{\equiv}CH$, $10^5\,k$, M^{-1} sec^{-1}
C_6H_6	2.5[a]	6.8[a]
C_6H_6:EtOH (75:25)	1.1[a]	
C_6H_6:EtOH (50:50)	0.55[a]	
EtOH	0.1[a]	0.1[b]
EtOH:H_2O (80:20)	0.2[b]	0.5[b]
EtOH:H_2O (50:50)	1.2[b] (1.5)[a]	2.7[b]
EtOH:H_2O (40:60)	1.8[a]	
EtOH:H_2O (50:50) buffered by 0.1 *M* Na_2CO_3	Very small [a,b]	Very small[a,c]
EtOH:H_2O (40:60) buffered by 0.1 *M* Na_2CO_3	Very small[a,b]	

[a] Rate constants were calculated from a decrease of perbenzoic acid. [b] Rate constants were calculated from a decrease of $RC_6H_4C{\equiv}CH$. [c] *m*-Bromophenylacetylene was used instead of *p*-methylphenylacetylene.

Peracid becomes its anion in aqueous ethanol buffered by Na_2CO_3, but the reaction of phenylacetylenes with perbenzoate ion was not appreciable, probably because the electrophilicity of acetylene is rather weak and the anion may spontaneously decompose faster than its attack on the triple bond.

Experimental Section

Materials.—*p*-Methoxyphenylacetylene,[18a] bp 110–114° (24 mm), and *m*-nitrophenylacetylene,[18b] bp 120–123° (24 mm) [lit.[18b] bp 118–120° (20 mm)], were synthesized from the corresponding cinnamic acids. Other substituted phenylacetylenes were prepared from the corresponding acetophenones.[19] Substituent and melting point or boiling point were *p*-Cl, mp 46.5–47.0°; *m*-Br, 96–98° (22 mm); *p*-Me, bp 70.0–70.5° (23 mm) [lit.[19] bp 79–81° (31–33 mm)]; and unsubstituted, bp 46.5–47.0° (20 mm) [lit.[20] bp 137–139° (760 mm)]. They were identified by their ir spectra,[21] their purities being checked by glc. Perbenzoic acid was prepared by the reaction of benzoyl peroxide with hydrogen peroxide[22] and recrystallized from hexane.

Kinetics.—The rate of consumption of PBA was followed iodometrically. The rate of consumption of phenylacetylenes was determined by glc, using anisole as an internal standard with a column (2 m) of 3 wt % Apiezon grease L on Celite 545 (80–100 mesh) and N_2 as a carrier gas (20 ml/min) at the starting temperature of 50°, which was elevated at a rate of 6°/min. An aliquot was removed and added to a known amount of anisole, and the remaining PBA was decomposed by addition of dimethyl sulfoxide. The resulting benzene solution was washed with aqueous $NaHCO_3$ to remove acidic components, dried (Na_2SO_4), and analyzed by glc. This procedure was done for a mixture of two kinds of phenylacetylenes with the reaction time between 0 and 48 hr, the relative rate constant (k_R/k_H) being calculated from this competitive reaction. Assuming rate constants for two kinds of phenylacetylenes to be k_A and k_B, their initial concentrations, a and b, and their consumed concentrations at a given time, x and y, respectively, the relative rate constant (k_A/k_B) is given by eq 3.

$$k_A/k_B = \ln\,[(a - x)/a]/\ln\,[(b - y)/b] \qquad (3)$$

Registry No.—PBA, 93-59-4

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Anodic Oxidations. V.[1] Aromatic Cyanation of Methoxydiphenylacetylenes

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Received March 27, 1972

We at first anticipated that, if the anodic oxidation of diphenylacetylene is conducted under the cyanation

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