Evidence for a Planar Transition State in Pericyclic Reactions Involving Acetylenes. A Hammett Study of the Thermal Cleavage of β-Hydroxyacetylenes[1a]

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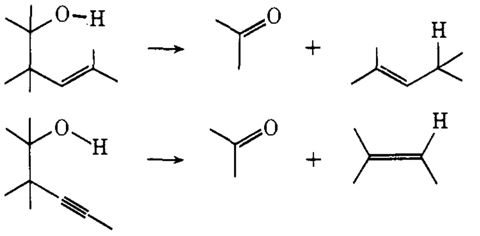
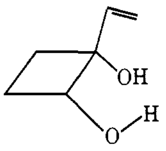
Abstract: The thermolysis of β-hydroxyacetylenes is reported to proceed through an intramolecular six-membered transition state in close analogy with the corresponding olefinic system. Aryl substituents at the C_1 position of both systems result in identical rate accelerations, relative to the corresponding phenyl derivatives. A ρ value of -0.35, in the range of 250–280°, was determined for both reactions. Lack of any electronic differences on rate accelerations in the two systems implicates steric factors for the previously reported differences in substituent effects in the two reactions. The data support the concept of a planar transition state for the acetylenes wherein electron delocalization is centered within the plane of that transition state. By contrast, a chair-like transition state is suggested for olefins wherein orbital overlap is centered in planes orthogonal to the median plane. The consistently higher reaction rate of acetylenic analogs may be the result of greater delocalization in the planar transition state or of greater nucleophilicity of the acetylene in a concerted but nonsynchronous process.

We have recently reported the results of a thermolysis study of β-hydroxyacetylenes.[2] The findings indicate the reaction to be a clean, homogeneous, unimolecular process which follows the first-order rate equation. These facts, together with a low activation energy and a substantial negative entropy of activation, implicate a concerted 1,5 sigmatropic hydrogen shift *via* a cyclic six-membered transition state, closely analogous to the corresponding reaction of β-hydroxyolefins.[3]



Surprisingly, the reaction of every acetylenic system included in our study proceeded at a rate faster than that reported for the corresponding olefin, despite the obvious additional energy requirement for the linear acetylenic system to lend itself to a cyclic six-membered ring. Furthermore, it was found that although substituents in the 1 and 2 positions accelerated the reactions of both systems, the degree of acceleration was smaller for the acetylenes by an amount which closely paralleled the rotational barrier about the C-1 to C-2 bond, as instigated by the substituents at these sites. Consequently, it was suggested that the transition state geometries for the two reactions differed, with that of the olefin being chair-like, while that of the acetylene appears planar.

The chair-like form for the olefin is in part dictated by the location of the participating π lobes, which are centered in a plane orthogonal to the potential transition plane. Such a preference is also indicated by the recent report of Conia and Barnier,[4] who find that although cleavage is the preferred mode of reaction in the thermolysis of a *trans*-2-vinyl-1-cyclobutanol (**1**), it is completely absent in the reaction of a cis analog (**2**), where such geometry is not feasible.



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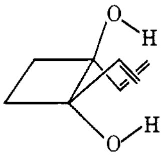

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The participating π lobes for the acetylenic species, however, can easily be centered in the transition plane itself as depicted in Figure 1. Note that all participating orbitals are centered in the same plane to afford maximum interaction and delocalization in the transition state. This geometry also represents the minimum required distortion from the preferred sp bond angle of 180° but does require eclipsing of substituents at C_1 and C_2. The present study was undertaken as a further test of the concept of differing transition state geometries in these two closely related reactions.

The effect of a phenyl substituent at C-1 of both olefinic and acetylenic systems was a rate increase in the olefinic case by a factor of 33, whereas the acetylenic rate increased only by a factor of 19. If the above analysis is correct, then this difference in rate accelerations is attributable solely to the steric interaction of the phenyl group with an eclipsed neighboring proton in the acetylenic transition state. No such steric inhibition applies to the chair-like olefinic transition state. Further substitution in the meta and para positions of the phenyl ring, however, cannot lead to any further steric contributions to the energetics of the respective transition states, and any such substituents should therefore bring about identical rate effects in both systems relative to the corresponding carbinols. If further

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(1) (a) Presented in part at the 4th Annual Northeast Regional Meeting of the American Chemical Society, Hartford, Conn., Oct 1972; (b) Northeastern University; (c) Universidad del Valle.

(2) A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, **93**, 6967 (1971).

(3) For a recent review, see G. G. Smith and F. W. Kelly, *Progr. Phys. Org. Chem.*, **8**, 191 (1971).

(4) J. M. Conia and J. P. Barnier, *Tetrahedron Lett.*, 4981 (1971).

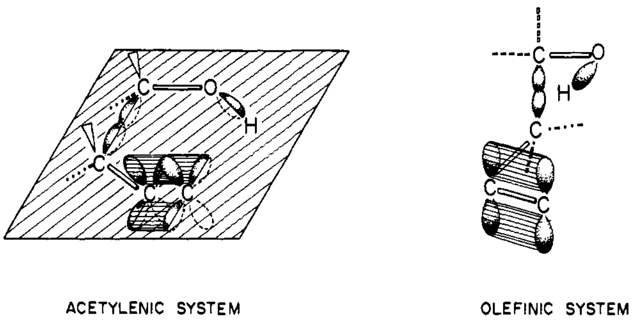

Figure 1. Schematic illustration of proposed transition-state geometry.

substitution on the phenyl rings does not bring about similar rate effects, then the two reactions are susceptible to different electronic factors and any conclusions regarding geometric transition state difference would be invalidated.

Results

Eight 1-aryl-3-butyn-1-ols were prepared *via* the reaction of the propargyl Grignard reagent with the appropriately substituted benzaldehyde, under conditions such that no allenic products are formed. Thermolyses were conducted in both a flow system, for product identification, and a static system, for the determination of kinetic parameters. The only reaction products observed were the expected para- or meta-substituted benzaldehyde and a volatile constituent whose vpc retention time was in agreement with that of allene.

As reported previously,[2] phenylbutynol thermolyzes too rapidly in the vapor state to permit monitoring of the reaction process by vpc. At temperatures sufficiently low to permit accurate analyses, the reactants are at best only incompletely vaporized. Consequently, the reactions were carried out in dilute solutions in an inert solvent, under conditions such that the material remained in the liquid phase throughout. The reaction in all cases followed the first-order rate equation for several half-lives, and the actual rate constants obtained are listed in the Experimental Section. The Arrhenius parameters[5] obtained are listed in Table I.

Table I. Arrhenius Parameters for Substituted 1-Phenyl-3-butyn-1-ols

Substituent	E_a, kcal/mol	Log A	$\Delta S^{\ddagger}$, eu, at 260°	Correlation coeff
None	36.2	11.2	−10.4	0.9998
p-Methyl	35.5	11.0	−11.3	0.9999
p-Chloro	36.3	11.2	−10.4	0.9999
p-Methoxy	35.0	10.9	−11.9	0.9998
p-Dimethylamino	36.0	11.4	−9.8	0.9998
m-Methyl	36.5	11.4	−9.7	0.9999
m-Chloro	36.3	11.2	−10.7	0.9999
m-Methoxy	36.1	11.2	−10.6	0.9997

Also listed are the correlation coefficients of the linear regression for each individual straight-line plot, to demonstrate the quality of the results.

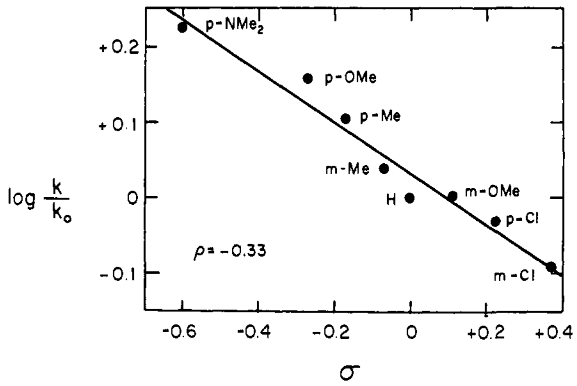

Figure 2. Hammett plot for thermolysis of 1-aryl-3-butyn-1-ols.

A Hammett plot of the rate constants,[6] at 260°, is shown in Figure 2. In all cases, the rate constant used, listed in Table II, was calculated from the corresponding Arrhenius plot and thus is based upon all kinetic determinations for that particular compound. The ρ value obtained is −0.33, as calculated by the method of least squares.

Table II. Rate Constants for Substituted 1-Phenyl-3-butyn-1-ols and 1-Phenyl-3-buten-1-ols at 260°

	Butynols Solution		Butenols Solution		Butenols Gas phase[a]
Substituent	10^4k, sec^{-1}	k/k_0	10^4k, sec^{-1}	k/k_0	10^4k, sec^{-1}
None	2.48	1.00	1.63	1.00	0.78
p-Methyl	3.12	1.26	2.07	1.27	1.23
p-Chloro	2.32	0.94	1.56	0.96	0.87
p-Methoxy	3.50	1.41	2.26	1.39	1.43
p-Dimethylamino	4.13	1.67			
m-Methyl	2.75	1.11	1.76	1.08	1.03
m-Chloro	2.02	0.81	1.26	0.77	
m-Methoxy	2.49	1.00	1.68	1.03	0.88

[a] Extrapolated values obtained from the data of ref 7.

A Hammett study of a similar olefin series in the gas phase has recently been reported.[7] Unfortunately, the temperature range utilized in that study was higher than could be realized in our experimental system. Since Hammett relationships obtained at widely differing temperatures are not necessarily comparable, it seemed desirable to repeat that study under the identical conditions utilized for the acetylenic series.

In order to minimize errors due to kinetic determinations at a single temperature, the thermolysis of each of seven arylbutenols was performed at three temperatures and the rate constants at 260°, listed in Table II, were obtained from the resultant Arrhenius plot. Despite the use of only three temperatures for each of these thermolyses, the data gave good straight-line plots, with correlation coefficients ranging from a low of 0.998 for the *p*-chloro derivative to a high of 0.99998 for the *p*-methyl. The Arrhenius parameters[5] obtained under these conditions are listed in Table III and, in the six compounds common to both studies, compare

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(5) All $\Delta S^{\ddagger}$ values reported herein are based on the formula $A = e(k/h)t_m e^{\Delta S^{\ddagger}/R}$ as urged by H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969). The energies and entropies of activation are estimated to be accurate to within ±1.5 kcal and ±2 eu, respectively.

(6) The σ values utilized were all taken from H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953). A later value for the *p*-dimethylamino group suggested by H. C. Brown and Y. Akamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958), gave a much poorer fit.

(7) G. G. Smith and K. J. Voorhees, *J. Org. Chem.*, **35**, 2182 (1970).

Table III. Arrhenius Parameters for Substituted 1-Phenyl-3-buten-1-ols

	Dilute Solution, 260°			Gas phase, 346° [a]		
Substituent	E_a	Log A	$\Delta S^{\ddagger}$	E_a	Log A	$\Delta S^{\ddagger}$
None	36.0	11.0	−11.6	37.1	11.1	−11.0
p-Methyl	35.8	11.0	−11.4	34.7	10.3	−14.5
p-Chloro	36.3	11.1	−11.1	36.3	10.8	−12.2
p-Methoxy	36.0	11.1	−11.0	34.3	10.2	−15.1
m-Methyl	36.9	11.4	−9.7	3.53	10.5	−13.8
m-Chloro	36.7	11.1	−10.8			
m-Methoxy	35.3	10.7	−21.8	36.9	36.9	−11.2

[a] Calculated from the data in ref 7 with the identical computer program utilized for other calculations reported herein.

favorably with those reported by Smith and Voorhees,[7] which are also listed. Unfortunately, the *p*-dimethylamino derivative failed to react cleanly, and the expected cleavage reaction was accompanied by considerable dehydration; consequently, this compound had to be omitted from the Hammett relation for the olefinic series.

In the absence of the *p*-dimethylamino derivative, the olefinic series gave a ρ of -0.358. If this derivative is also omitted from acetylenic series, then its ρ value becomes -0.351. It is of interest to note that the ρ value obtained by Smith and Voorhees[7] for virtually the same olefinic series, but in the gas phase and at 346°, was -0.26, which differs but slightly from the one reported herein in solution and at 260°. Furthermore, the ρ value found is larger at the lower temperature, as is to be expected.

Discussion

Alkyl substituents on the 1 and 2 positions of 3-buten-1-ols accelerate the thermal retro-ene cleavage.[8] Such substituents also accelerate the analogous cleavage of 3-butyn-1-ols, but not as much as in the former case. That the differences in accelerating effects are due to steric inhibition of the acetylenic transition state is borne out by this study. The 1-phenyl substituent can be expected to introduce as much steric interference, due to eclipsing with a neighboring proton, as can be expected from a similarly positioned meta- or para-substituted phenyl group, since such further aromatic substituents are considerably removed from the interfering site. The Hammett studies described above afforded identical ρ values for the 1-aryl substituted butynols and butenols. Furthermore, a comparison of the ratio k/k_0 for identical substituents in the two series (see Table II) confirms the fact that aryl substituent effects are identical in both series and the similarities in ρ values obtained are not fortuitous results of differently scattered points in the Hammett plots. Indeed, Figure 3 illustrates the linear free energy relationship between the two reactions. The slope of this experimental line, calculated by the method of least squares, is 1.03 and thus differs by only 3% from the theoretical slope corresponding to perfect matching of aromatic substituent effects in the two reactions. The conclusion seems inescapable that *if substituent effects are identical in the two systems in the absence of steric interference, then the differences in previously noted effects must indeed be the resultant of steric factors alone.* Thus, the results of this study support the previously stated concepts of differing transition state geometries for the two reactions.

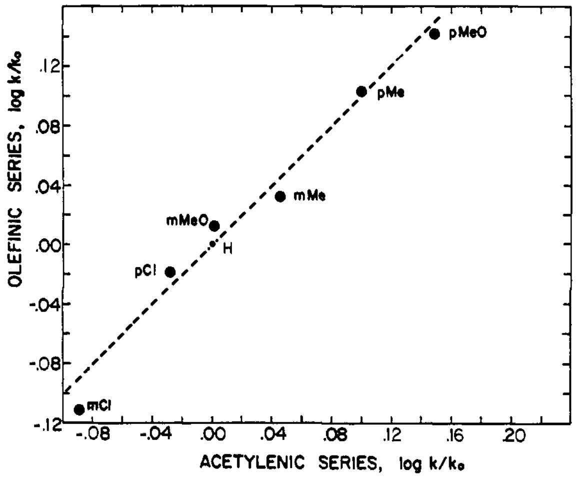

Figure 3. Linear free energy relationship for thermolyses of 1-arylbutenols and 1-arylbutynols.

An examination of the data of Table II indicates that acetylenic alcohols react faster than their olefinic analogs by a surprisingly constant factor of 1.53 ± 0.05. These data are in accord with our previous results in the alkyl substituted series, wherein acetylenic bond participation always results in a higher reaction rate.[2] Although we readily admit the striking similarities in activation parameters between acetylenic and olefinic analogs, as has been pointed out by Kwart and Latimore,[9] it does seem curious that the acetylenes always proceed at a faster rate. The acetylenic system must involve an energy term to compensate for the distortion of the linear sp system as well as a term for eclipsing hydrogens and/or substituents at C-1 and C-2. One possibility for the faster rate in the acetylenic system, despite the additional energy increments, is that the transition state geometry, as depicted in Figure 1, permits a greater degree of delocalization as opposed to the nonplanar olefinic transition state.

A second possibility for the faster acetylenic rates arises from a consideration of medium effects as illustrated by a comparison of columns 4 and 6 of Table II and supplemented by the data recapitulated in Table IV.

Table IV. Medium Effects on Thermolysis Rates of 3-Butyn-1-ols[a] ($10^5 k_{260°}$)

Substituent	Gas phase (extrapolated)	Xylene (dil soln)	Liquid phase (extrapolated)
None	0.818	1.88	2.86
1-Ethyl	1.80		9.4
1,1-Dimethyl	2.03	3.42	5.3

[a] From ref 2. For the purpose of emphasis, these compounds are named as derivatives of the parent alcohol.

In all cases for which data are available, both butenols and butynols react faster in dilute solution than in the

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(8) G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

(9) A maximum isotope effect has been reported for the thermolyses of both but-3-en-1-ol-*O-d* and but-3-yn-1-ol-*O-d* by H. Kwart and M. C. Latimore, *J. Amer. Chem. Soc.*, 93, 3770 (1971). These investigators have interpreted their results as indicative of a symmetrical transition state, although the utility of the deuterium isotope effect as a criterion for transition state symmetry has been questioned.[10]

(10) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, 93, 512 (1971).

Table V. Physical Data for 1-Aryl-3-butyn-1-ols

Substituent	Bp, °C (mm)	n^tD	Yield, %	Formula	Analysis, %	
					Calcd	Found
p-OMe[a]	118 (0.9)[b]	1.5495^{22}	55	$C_{11}H_{12}O_2$	C, 74.97; H, 6.87	C, 75.05; H, 6.87
p-Cl	102 (1.0)[c]	1.5576^{22}	29	$C_{10}H_9ClO$	C, 66.49; H, 5.02	C, 66.23; H, 5.35
p-NMe₂[a]	145 (2.0)	1.5761^{27}	51	$C_{12}H_{15}NO$	C, 76.15; H, 7.99	C, 75.97; H, 7.98
p-Me	95 (1.1)	1.5390^{23}	29	$C_{11}H_{12}O$	C, 82.46; H, 7.55	C, 82.61; H, 7.53
m-OMe	122 (1.0)	1.5469^{27}	47	$C_{11}H_{12}O_2$	C, 74.97; H, 6.87	C, 74.90; H, 6.94
m-Cl	105 (1.3)	1.5554^{25}	52	$C_{10}H_9ClO$	C, 66.49; H, 5.02	C, 66.54; H, 5.09
m-Me	92 (1.1)	1.5379^{22}	47	$C_{11}H_{12}O$	C, 82.46; H, 7.55	C, 82.51; H, 7.57

[a] On vpc, both the *p*-OMe and *p*-NMe_2 compounds gave two poorly resolved peaks, typical of decomposition of the alcohol in both the column and the injection port. Analysis and spectral data, however, indicated only the alcohol to be present in each of these samples. [b] Lit. 115° (0.5 mm): P. Läuger, M. Prost, and R. Charlier, *Helv. Chim. Acta*, **42**, 2379 (1959). [c] Lit.[b] 103–106° (0.2 mm).

Table VI. Thermolysis Rates (10^4k, sec^{-1})

Temp, °C	H	*p*-Me	*p*-Cl	*p*-OMe	*p*-NMe₂	*m*-Me	*m*-Cl	*m*-OMe
			A. Substituted 1-Phenyl-3-butyn-1-ols					
280	8.54	10.4	7.93	11.5	14.1	9.45	6.94	8.50
270	4.53	5.71	4.35	6.30	7.62	5.06	3.70	4.62
260	2.48	3.10	2.28	3.52	4.04	2.74	2.00	2.42
250	1.28	1.63	1.20	1.83	2.16	1.40	1.04	1.30
			B. Substituted 1-Phenyl-3-buten-1-ols					
285	7.44							
280	5.50	6.97	5.42	7.58		6.17	4.34	5.61
270	2.97	3.84	2.82	4.22		3.26	2.39	3.00
260		2.05	1.57	2.22		1.75	1.24	1.68
250	0.846							

gas phase, and the reaction proceeds still more rapidly in the neat liquid phase. This effect, coupled with the small negative ρ value for both systems, could be indicative of a small lag in carbon–carbon bond rupture behind the initial hydrogen transfer step. Although activation energy and entropy terms clearly implicate concerted processes, such processes need not necessarily be synchronous.[11] The development of a small positive charge at C-1 would be in line with a proton transfer whose progress slightly precedes that of C–C bond rupture.[12] The increased rate of the acetylenic system may then result from the reported higher nucleophilicity of the acetylenic bond toward a proton compared with an analogous olefinic system.[13]

An evaluation of the two above possibilities, if indeed either is applicable, must await the outcome of further work in progress, wherein the hydrogen transfer is not from an intrinsically polar heteroatom but instead comes from a site which is directly susceptible to a Hammett probe.

Experimental Section

Boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer PE-21 spectrophotometer on neat liquid samples. Nmr spectra were determined with a Varian A-60A spectrometer using tetramethylsilane as an internal standard. Elementary analyses were performed by the late Dr. Stephen M. Nagy, Belmont, Mass., or by Spang Microanalytical Laboratory, Ann Arbor, Mich. Refractive indices were determined on a Bausch and Lomb Abbe refractometer. Vapor phase chromatographic analyses were obtained with an F&M Model 500 using 2-ft columns packed with 10% silicone grease on Chromosorb P. Relative peak areas were determined with a Disc integrator.

Preparation of 1-Aryl-3-butyn-1-ols. All of these alcohols were prepared from the propargyl Grignard reagent and the appropriately substituted benzaldehyde. The preparation of 1-(*p*-methoxyphenyl)-3-butyn-1-ol follows as a typical example.

A 500-ml, three-necked flask, equipped with a mechanical stirrer, Friederich's condenser, thermometer, and addition funnel, was charged with 12 g (0.5 mol) of Mg turnings, 100 ml of anhydrous ether, previously dried over sodium wire, 0.5 g of freshly distilled propargyl bromide, and 0.1 g of $HgCl_2$. The mixture was stirred and gently refluxed on a steam bath for 45 min, at which time the magnesium had been activated as evidenced by cloudiness of the solvent. The steam bath was removed and the reaction vessel was cooled in a Dry Ice-acetone bath. The remaining bromide (a total of 23 g, 0.2 mol, was used) was diluted with 75 ml of anhydrous ether and added dropwise to the stirring mixture at a rate such that the temperature inside the vessel was maintained between −25 and −17°. Total time for addition was 2 hr. The internal temperature was then raised to 10°, at which point a solution of freshly distilled *p*-anisaldehyde, 17.7 g (0.13 mol), in 75 ml of anhydrous ether was added dropwise to the stirring mixture. The temperature was maintained between +5 and +15° during the addition which required 1 hr. After completion of addition, the cooling bath was removed and the mixture was allowed to attain ambient temperature. The liquid was then decanted into an ice–NH_4Cl mixture and allowed to stand overnight. The two phases were separated and the aqueous phase was extracted with two 25-ml portions of ether. The ether extracts were combined with the organic phase and the resulting solution was washed with three 25-ml portions of water. This solution was dried over $MgSO_4$ and filtered. Fractional distillation of the filtrate under reduced pressure afforded 13.0 g (55% yield based on aldehyde) of the desired alcohol. Physical data for the arylbutynols are given in Table V. The infrared spectra (neat liquid) of all the arylbutynols contained a typical strong OH peak at 3400–3500 cm^{-1} with a sharp spike at 3300 cm^{-1} ($\equiv$C—H) and a weak band at 2120 ± 10 cm^{-1} (C$\equiv$CH). None showed any absorption in the allene region. Similarly, all of the arylbutynols showed bands in their nmr spectra consistent only with a terminal

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(11) For a review of the concepts of synchronous *vs.* nonsynchronous concerted reactions, see J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970); L. Salem, *Accounts Chem. Res.*, **4**, 322 (1971).

(12) The transition states involved in these reactions must possess intrinsic polar character due to the heteroatom present within the involved bonding system. K. Humski, R. Malojčić, S. Borčić, and D. E. Sunko, *J. Amer. Chem. Soc.*, **92**, 6534 (1970), have presented evidence that even in the nonpolar Cope rearrangement there appears to be a lag between bond-forming and bond-breaking processes. It might be of interest to note that A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970), have found a MINDO/2 calculation for the Cope transition state to give a low activation energy for the process. This value appears to be in the expected direction if that state is not symmetrical as assumed, *i.e.*, if overlap integrals at C-1–C-6 are not as large as for C-3–C-4 in the transition state.

(13) A. A. Petrov and Yu. I. Porfir'eva, *J. Gen. Chem. USSR*, **33**, 3142 (1963).

acetylene, δ 2.0 ± 0.1 (1 H, t, J = 2.5 Hz), and none absorbed in the allene region.

Preparation of 1-Aryl-3-buten-1-ols. These alcohols were prepared from the reaction of the allyl Grignard reagent with the appropriately substituted benzaldehyde, following essentially the procedure of Smith and Voorhees.[7] All arylbutenols utilized are fully described in the above reference, with the sole exception of the following compound.

1-*m*-Chlorophenyl-3-buten-1-ol. This compound was isolated, in 38% yield, by distillation of the crude material resulting from the above procedure,[7] bp 99° (0.2 mm), $n^{22}\mathrm{D}$ 1.543.

Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.75; H, 6.07. Found: C, 65.88; H, 6.12.

Kinetic Procedures. The method used for following the thermolysis rates of the 1-aryl-3-butyn-1-ols and 1-aryl-3-buten-1-ols was exactly as previously described, method A, ref 2. Tetralin was used as the internal standard for all the alcohols with the exception of 1-(*m*-methoxyphenyl)-3-butyn-1-ol, for which *p-tert*-butyltoluene was used. A run with 1-phenyl-3-butyn-1-ol using *p-tert*-butyltoluene as an internal standard gave a rate of 4.44×10^{-4} sec^{-1} at 270° compared with 4.53×10^{-4} sec^{-1} using tetralin as an internal standard.

The reaction was shown to be independent of starting concentration. For example, 1-phenyl-3-buten-1-ol was thermolyzed at 270° in xylene solution at 1, 4, and 10% (v/v) to give rate constants of 3.04, 2.97, and 3.06×10^{-4}, respectively. Reaction homogeneity was established by packing a tube with thin capillaries such that the surface area was increased by a factor of at least five. Under such conditions the above alcohol afforded a rate constant of 2.9×10^{-4}. The rate constants obtained are listed in Table VI.

Phase-Transfer Catalysis. II. Kinetic Details of Cyanide Displacement on 1-Halooctanes

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Contribution from the Chemicals Research Division, Continental Oil Company, Ponca City, Oklahoma 74601. *Received August 5, 1972*

Abstract: Displacement reactions of alkyl halides in an organic phase with anions in an aqueous phase that are inhibited because of phase separation may often be strongly catalyzed by addition of small amounts of tetraalkylammonium or tetraalkylphosphonium salts. This ability of organic-soluble cations to function as *phase-transfer* catalysts was further explored to determine kinetics and characteristics of the system. Evidence is presented to show that catalysis is directly proportional to the amount of quaternary salt present in the organic phase, that the rate is first order in 1-haloalkane concentration, and that the rate is not dependent on stirring speed beyond just enough to obtain moderate mixing (*ca.* 250 rpm). Displacement depends strongly on the aqueous-phase cyanide ion/chloride ion ratio, since this affects the equilibrium position for transfer of cyanide into organic phase by quaternary salt. The anion transfer equilibrium constant is sensitive to the amount of water present, the relative concentrations of NaCN and NaCl, and the polarity of the organic phase, probably because cyanide ion tends to be more highly hydrated than chloride. The quaternary salts used as catalysts aggregate only to a low degree (1.5–3 at 0.1 *M*) in anhydrous nonpolar solvents. These data are consistent with the proposed ability of the organic-soluble cations to repeatedly bring anions into the organic phase where displacement occurs, probably without participation of micelles.

Phase-transfer catalysis, introduced and qualitatively described in a previous report,[1] is further described here relative to the kinetics of cyanide displacement on 1-chloro- and 1-bromooctane. Phase-transfer catalysis is applicable to reactions which are inhibited because of the inability of the reagents to physically come together. For example, in the reaction between aqueous sodium cyanide and 1-chlorooctane, addition of an organic-soluble quaternary ammonium or phosphonium salt catalyzes cyanide displacement on RCl. As illustrated by eq 1, the function of the quaternary salt, QX, is to bring cyanide ion into the organic phase in a form suitable for reaction with RCl and return the displaced chloride ion to the aqueous phase where QCN can be regenerated. The previous paper[1] and other reports[2] show a number of applications using quaternary ammonium or phosphonium salts as phase-transfer catalysts. An important assumption in systems described by eq 1 is that the rate-determining step of the reaction takes place in the organic phase of the reaction mixture rather than in the aqueous phase, at the interface, or in micelles. Experimental evidence to support this assumption and kinetics and general physical details of the Q$^+$-catalyzed NaCN(aq)/RCl(org) reaction are presented here.

$$\begin{tikzcd} \mathrm{RCl} + \mathrm{QCN} \arrow[r] & \mathrm{RCN} + \mathrm{QCl}\ \text{(organic phase)} \arrow[d] \\ \mathrm{NaCl} + \mathrm{QCN} \arrow[u] \arrow[r, leftrightarrows] & \mathrm{NaCN} + \mathrm{QCl}\ \text{(aqueous phase)} \end{tikzcd} \qquad (1)$$

Results and Discussion

1. Evidence That Displacement Occurs in the Organic Phase.

Much work has been reported[3,4] showing that cationic surfactants substantially catalyze reactions between certain anions and organic substrates with close correlation between rate enhancement and micelle formation. Since the quaternary salts used in phase-transfer catalysis are similar to those used in micelle-catalyzed reactions, it is necessary to determine whether the cyanide attack on RCl takes place in the organic phase, in the aqueous phase, in micelles, or at the interface.

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