ether fractions were washed with water until the water filtrate was neutral and then dried over anhydrous Na_2SO_4. Filtration and concentration under reduced pressure left 6.5 g of an oil that was distilled, bp 120–135° (0.3 mm), to give **27**: 4.3 g (43%); nmr ($CDCl_3$) δ 7.6–7.0 (m, 5, ArH), 4.67 (d, 2, J = 4 Hz, $=CH_2$), 2.16 (s, 3, NCH_3).

Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.24; H, 9.33; N, 5.73.

This oil **27** was further characterized as the hydrochloride, mp 208–209° dec.

Anal. Calcd for $C_{17}H_{23}N \cdot HCl$: C, 73.49; H, 8.71; N, 5.04. Found: C, 73.12; H, 8.98; N, 5.06.

Acknowledgment. We wish to acknowledge the support and encouragement of Dr. George deStevens and Mr. L. Dorfman, whose staff we thank for microanalyses and spectra. We also wish to thank Mrs. M. Brzechffa for assistance in collection of the X-ray data.

Registry No.—**3a**, 25012-72-0; **3b**, 13221-89-1; **5a**, 50640-99-8; **5a** hydrochloride, 50641-00-4; **5b**, 50641-01-5; **6a**, 50641-02-6; **6b**, 50641-03-7; **7**, 50641-04-8; **8a**, 50641-05-9; **8b**, 50641-06-0; **9**, 50640-72-7; **10**, 50640-73-8; **11**, 50641-07-1; **12**, 50641-08-2; **12** hydrochloride, 50641-09-3; **17**, 19608-59-4; **18**, 50640-74-9; **18** methobromide, 50640-75-0; **19**, 50640-76-1; **20**, 50640-77-2; **21** hydrochloride, 50640-78-3; **22** hydrochloride, 50640-79-4; **23**, 50640-80-7; **23** maleate, 50640-81-8; **24**, 50640-82-9; **24** maleate, 50640-83-0; **25** maleate, 50640-85-2; **26** hydrochloride, 50640-86-3; **26** picrate, 50790-98-2; **27**, 50640-87-4; **27** hydrochloride, 50640-88-5; 1,3,4,7,8,8a-hexahydro-6-hydroxy-6-(*m*-methoxyphenyl)-2-methylisoquinoline, 50790-99-3.

Supplementary Material Available. A table with the final atomic positional and thermal parameters and a figure with bond angles and bond lengths will appear following these pages in the microfilm edition of this volume of the journal. The standard deviations and observed structure factors are no longer available. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-1118.

References and Notes

(1) V. Boekelheide and W. M. Schilling, *J. Amer. Chem. Soc.*, **72**, 712 (1950).
(2) S. M. McElvain and D. C. Remy, *J. Amer. Chem. Soc.*, **82**, 3960 (1960).
(3) E. L. May and L. J. Sargent in "Analgetics," G. deStevens, Ed., Academic Press, New York, N. Y., 1965, Chapter IV.
(4) E. Wenkert, K. G. Dave, and R. V. Stevens, *J. Amer. Chem. Soc.*, **90**, 6177 (1968).
(5) S. M. McElvain and P. H. Parker, *J. Amer. Chem. Soc.*, **78**, 5312 (1956).
(6) G. H. Posner, *Org. React.*, **19**, 1 (1972).
(7) S. Sicsic and N. Luong-Thi, *Tetrahedron Lett.*, 169 (1973).
(8) We are grateful to Professor Virgil Boekelheide for a sample of his original picrate, prepared more than 25 years ago!
(9) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965, p 87.
(10) As was pointed out by a referee, **18** is probably a mixture of both conformers. An approximate calculation suggests a 2:1 mixture of **18a** and **18b**.
(11) Melting points were obtained in a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were obtained with Perkin-Elmer spectrophotometers, Models 21 and 521. Nmr spectra were obtained with a Varian A-60 nmr instrument. Mass spectra were obtained with an AEI MS 902 mass spectrometer at 70 eV.

Reaction of Acetylenes with Hydrogen Chloride in Acetic Acid. Effect of Structure upon AdE2 and Ad3 Reaction Rates

Robert C. Fahey,* Michael T. Payne, and Do-Jae Lee

Department of Chemistry, University of California, San Diego, La Jolla, California 92037

Received August 13, 1973

Studies of the initial reaction rate and product composition for the reaction of phenylacetylene, 1-phenylpropyne, 1-hexyne, and *tert*-butylacetylene with HCl in HOAc at 25° are reported. The stereochemistry of HCl addition to 1-hexyne-*1-d* at 50° was also examined. The results are found to be consistent with reaction *via* competing AdE2 and anti Ad3 reaction mechanisms. The results show that the AdE2 and Ad3 mechanisms involve different regiospecificity, as well as stereospecificity. The effect of structure upon reaction rate is found to be quite different in the two mechanisms, implicating significantly different transition-state structures.

In previous papers[1-6] we have presented evidence for two distinct mechanisms for addition of HCl to olefins and acetylenes in acetic acid. Reaction *via* the AdE2 mechanism[1-3] occurs by slow protonation of the unsaturated compound to form a carbonium chloride ion pair in-

olefin (acetylene) + HCl ⟶ $[R^+Cl^-]$ ⟶

RCl + ROAc ⟶ (ketone)

termediate which collapses to a mixture composed mainly of chloride and some acetate, the vinyl acetates formed from acetylenes undergoing a rapid subsequent reaction to form a ketone. The rate of reaction depends upon unsaturated reactant and HCl concentrations, but the ratio of the RCl to ROAc is not influenced by the HCl concentration. Moreover, the presence of chloride salt does not increase the percentage of RCl formed and, at 0.2 *M*, causes a less than threefold rate increase. This shows that, once formed, the ion-pair intermediate collapses rapidly to a product mixture determined solely by the structure of the ion pair and not significantly influenced by the composition of the external reaction solution. The effect of salt upon the rate results from a salt effect upon the rate of formation of the carbonium ion pair. Styrene and *tert*-butylethylene react exclusively *via* this mechanism.[3]

Other olefins and acetylenes exhibit different behavior under the same reaction conditions. Thus, the ratio of RCl to ROAc obtained from 3-hexyne[2] and also from cyclohexene[4,5] varies with the HCl concentration. The presence of chloride salt not only markedly increases the ratio of RCl to ROAc but gives rise to a rate increase indicative of catalysis by chloride ion. Under these conditions addition occurs with anti stereochemistry. The observations imply that an Ad3 addition, formally the reverse of E2 elimination, is involved.

The reaction of 1,2-dimethylcyclohexene has been found to involve AdE2 addition, giving largely syn HCl adduct, at low HCl concentration, but in the presence of chloride salt a more rapid anti Ad3 addition of HCl dominates.[6]

An understanding of how structure influences reactivity in each of these mechanisms is important in designing synthetic procedures and also in understanding the electronic structure of the transition states. We report here

studies designed to provide information concerning the effect of structure upon reactivity for reaction of acetylenes with HCl in HOAc. Stereochemistry of addition and the effect of chloride salt upon rate and product composition are employed as the criteria of mechanism.

Experimental Section

An Aerograph Model 200 gas chromatograph equipped with thermal conductivity detectors and a Disc integrator was employed for all glpc analyses. Chromosorb P (acid washed) was used as solid support. Pmr spectra were measured on a Varian T-60 spectrometer as approximately 15% v/v solutions in CCl_4; chemical shifts are reported in parts per million downfield from tetramethylsilane as internal standard.

Materials. Acetophenone, 1-phenyl-2-propanone, *p*-xylene, chlorobenzene, and pinacolone were obtained from Matheson Coleman and Bell. Phenylacetylene, 1-phenylpropyne, and 1-hexyne were obtained from Farchan and purified by vacuum distillation on a spinning band column. These purified acetylenes and *tert*-butylacetylene (Farchan) were shown to be ≥99.9% pure by analytical glpc. Samples of (*Z*)- and (*E*)-2-chloro-1-phenylpropene were prepared as described previously.[7] A sample of 2,2-dichlorohexane was obtained from the reaction of 2-hexanone with PCl_5;[8] the product was first purified by vacuum distillation through a glass helix column and then by preparative glpc. All other materials were as described in previous studies.[1,2]

Preparation of 1-Hexyne-*1-d*. A 3 *M* ethereal solution (250 ml) of methylmagnesium bromide (Arapahoe) was added dropwise with stirring to 30 g of 1-hexyne in 50 ml of ether, after which the mixture was refluxed for 3 hr. The mixture was cooled to 0°, 60 ml of D_2O was added, the mixture was stirred for 2 hr, and 100 ml of 2.5 *M* HCl was added. An additional 100 ml of ether was added and the ether layer was separated, dried over anhydrous $MgSO_4$, and concentrated by removal of ether through a Vigreux column. Spinning-band distillation of the concentrated ether fraction yielded 14 g of 1-hexyne-*1-d*, bp 70.5–71.0°, found by glpc to be 99.6% pure (0.4% ether) and by pmr to contain ≥98% deuterium at C-1.

Addition to Phenylacetylene. Reaction mixtures containing 0.8 *M* phenylacetylene, 0.75 *M* HCl, and 0.039 *M* 1-phenyl-2-propanone (internal standard) were prepared with and without tetramethylammonium chloride (TMAC) (0.2 *M*) in volumetric flasks as described previously and placed in a 25° thermostated bath. Samples (5 ml) were withdrawn at intervals and quenched by mixing with 25 ml of 10% aqueous NaCl and 10 ml of pentane. The aqueous fraction was washed with two 5-ml portions of pentane; the combined pentane fractions were washed with 10 ml of 10% aqueous $NaHCO_3$ and dried over anhydrous K_2CO_3. The pentane fraction was concentrated by evaporation and analyzed by glpc on a 0.125-in. column packed with 20% SE-52 (first 4 ft) and 20% DEGS (last 8 ft) operated at 150° with a helium flow rate of 15 ml/min. Retention times in minutes follow: phenylacetylene, 4; α-chlorostyrene, 9; acetophenone, 14.5; 1-phenyl-2-propanone, 18. Initial rates and product compositions were determined at 1–9% conversion. The two major products were isolated by preparative glpc from a sample of a reaction mixture without added TMAC at near complete reaction. The pmr spectrum of the major product was identical with that of authentic α-chlorostyrene, while the pmr spectrum of the minor product was identical with that of authentic acetophenone. Calibrations with the internal standard accounted for 95–100% of the starting acetylene as product or recovered starting material.

Addition to 1-Hexyne. Reaction solutions were prepared and reaction samples were worked up in the same fashion as described previously[1,2] for addition to 3-hexyne; *p*-xylene was employed as an internal standard. Analysis by glpc was carried out on a 25 ft × 0.125 in. 10% XF1150 column operated at 100° and 13 ml/min of helium. Retention times in minutes follow: 1-hexyne, 6; (*Z*)-2-chloro-2-hexene and 2-chloro-1-hexene, 10; (*E*)-2-chloro-2-hexene, 13; *p*-xylene, 23; 2,2-dichlorohexane, 27; 2-hexanone, 29. Quantitative measurements were made at 1–9% conversion (Figure 1).

Products were isolated by preparative glpc from runs at higher temperatures so that significant conversion could be obtained in reasonable time periods. Reaction of 0.87 *M* 1-hexyne with HCl (0.82 *M*) in the presence of TMAC (0.42 *M*) at 50° for 6 days gave 60% conversion of 1-hexyne. Samples of 2-chloro-1-hexene, (*E*)-2-chloro-2-hexene, 2,2-dichlorohexane, and 2-hexanone were isolated from the product mixture and their pmr spectra were measured. The spectrum of 2-hexanone proved to be identical with

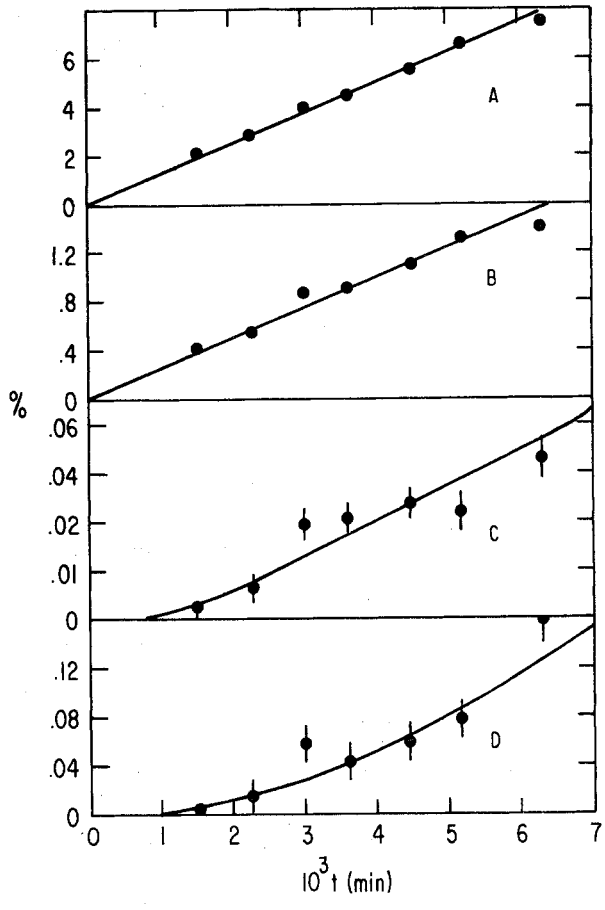


Figure 1. Appearance of products as a function of time in the reaction of 1-hexyne (0.8 *M*) with HCl (0.75 *M*) in the presence of TMAC (0.2 *M*) at 25.0° in HOAc: (A) 2-chloro-1-hexene plus (*Z*)-2-chloro-2-hexene; (B) 2-hexanone; (C) (*E*)-2-chloro-2-hexene; (D) 2,2-dichlorohexane. Solid lines represent the calculated values (see text).

that of an authentic sample. Pmr spectral data for 2-chloro-1-hexene in CCl_4 exhibited a narrow multiplet (δ 5.10, 2 H), a broad triplet (δ, 2.35, 2 H, J = 7 Hz), a multiplet (δ 1.2–1.7, 4 H), and an unsymmetrical triplet (δ 0.93, 3 H). In benzene the spectrum gave a doublet (δ 5.05, 1 H, J = 1 Hz), an approximate quartet (δ 4.82, 1 H, J = 1 Hz), a broad triplet (δ 2.13, 2 H, J = 7 Hz), a multiplet (δ 1.0–1.6, 4 H), and another multiplet (δ 0.77, 3 H). The pmr spectrum (CCl_4) of (*E*)-2-chloro-2-hexene consisted of a broad triplet (δ 5.58, 1 H, J = 2 Hz), a broad singlet overlapping a multiplet (δ 2.05 and 2.0, 5 H), a sextet (δ 1.43, 2 H, J = 7 Hz), and an unsymmetrical triplet (δ 0.93, 3 H, J = 7 Hz). The pmr spectrum of 2,2-dichlorohexane showed a multiplet (δ 2.18, 2 H), a singlet (δ 2.13, 3 H), a multiplet (δ 1.2–1.8, 4 H), and an unsymmetrical triplet (δ 0.98, 3 H, J = 7 Hz). A sample (30% of product) consisting of 95% (*Z*)-2-chloro-2-hexene and 5% 2-chloro-1-hexene was isolated by glpc from a reaction of 0.8 *M* 1-hexyne with 0.8 *M* HCl at 125° for 4 days; the pmr spectrum of the major isomer exhibited a broad triplet (δ 5.43, 1 H, J = 7 Hz), a broad doublet (δ 2.14, 2 H, J = 7 Hz), a doublet (δ 2.10, 3 H, J = 1 Hz), a broad sextet (δ 1.43, 2 H, J = 7 Hz), and an unsymmetrical triplet (δ 0.94, 3 H, J = 7 Hz). For reactions carried to >50% conversion at 50°, calibration with internal standard showed that ≥97% of the initial 1-hexyne was accounted for as products or unreacted starting material.

Addition to 1-Hexyne-*1-d*. Reactions of 1-hexyne-*1-d* (0.8 *M*) with HCl (0.75 *M*) in the presence and absence of TMAC (0.2 *M*) were conducted in ampoules at 50° for 2–3 weeks. The peak corresponding to 2-chloro-1-hexene was isolated by preparative glpc and the pmr spectrum was determined in benzene as solvent. The relative amounts of syn and anti adduct were determined from the ratio of the peak areas for the resonances at 5.05 and 4.82 ppm.

Addition to 2-Hexyne. Reaction of 2-hexyne (0.9 *M*) with HCl (0.8 *M*) in the presence of TMAC (0.4 *M*) in a sealed ampoule at 50° was allowed to proceed for 6 days and then worked up. Analysis by glpc as described for addition to 1-hexyne indicated ~75%

Table I
Initial Rates and Product Composition for the Reaction of Acetylenes (0.8 *M*) with HCl (0.75 *M*) in Acetic Acid at 25° in the Absence and Presence of TMAC

Registry no.	Acetylene	[TMAC], *M*	10^7 *R*, *M* sec^{-1}	Products (%) Chloride	Products (%) Ketone
536-74-3	PhC≡CH	0	79	**1** (92)	**2** (8)
		0.2	174	**1** (88)	**2** (12)
693-02-7	1-Hexyne	0	0.29	**3** (35)	**4** (65)
		0.2	2.2	**3** (82)	**4** (18)
917-92-0	*tert*-Butylacetylene	0	0.094	**8** (26)	**9** (74)
		0.2	0.48	**8** (75)	**9** (25)
928-49-4	3-Hexyne[a]	0	0.87	(47)[b]	3-HO[c] (53)
		0.21	16.7	(96)[b]	3-HO[c] (4)

[a] From ref 2; 0.81 *M* 3-hexyne, 0.78 *M* HCl. [b] *trans*-3-Chloro-3-hexene. [c] 3-Hexanone; ≤1% *cis*-3-chloro-3-hexene formed.

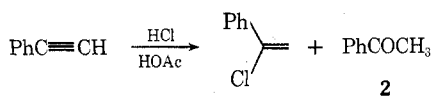
conversion of 2-hexyne with a peak having a retention time identical with that of 2-chloro-1-hexene accounting for 97% of the product. The pmr spectrum of material obtained by glpc purification of the major product peak was consistent with an equal mixture of (*E*)-2-chloro- and (*E*)-3-chloro-2-hexene. Comparison with the spectrum of the 2-chloro-2-hexene obtained from reaction of 1-hexyne with HCl at 125° (see above) gave rise to an nmr assignment for (*E*)-3-chloro-2-hexene having a broad quartet (δ 5.48, 1 H, *J* = 7 Hz), a broad triplet (δ 2.27, 2 H, *J* = 7 Hz), a doublet (*J* = 7 Hz) of triplets (*J* = 1 Hz) (δ 1.73, 3 H), a multiplet (δ 1.46, 2 H), and an unsymmetrical triplet (δ 0.92, 3 H, *J* = 7 Hz).

Addition to *tert*-Butylacetylene (3,3-Dimethyl-1-butyne). Reaction solutions were prepared and worked up as described for 1-hexyne but using chlorobenzene as internal standard. Analysis by glpc was carried out on a 25 ft × 0.125 in. 10% XF1150 column operated at 97° and 12 ml/min of helium. Retention times in minutes follow: *tert*-butylacetylene, 4; 2-chloro-3,3-dimethyl-1-butene, 6.5; pinacolone, 14; chlorobenzene, 27. Two unidentified minor products with retention times of 10 and 23 min were observed at less than 10% conversion and contributed about 2 and 3.5%, respectively, of the total product. The two major products were isolated from a reaction of *tert*-butylacetylene (0.8 *M*) with HCl (0.75 *M*) carried out in a sealed ampoule at 50° for 3 weeks. The pmr spectrum of glpc-purified product with 6.5-min retention time (2-chloro-3,3-dimethyl-1-butene) exhibited an AB multiplet at 5.09 ppm (2 H) and a singlet at 1.17 ppm (9 H). The pmr spectrum of the product with 14-min retention time was identical with that of authentic pinacolone.

Addition to 1-Phenylpropyne. Reaction mixtures were prepared and worked up as described previously.[1,2] Analysis by glpc was conducted on a 25 ft × 0.125 in. 20% XF1150 column operated at 170° and 18 ml/min of helium. Retention times in minutes follow: 1-phenylpropyne, 12.5; (*E*)-1-chloro-1-phenylpropene, 17.5; (*E*)-2-chloro-1-phenylpropene, 20; (*Z*)-1-chloro-1-phenylpropene, 22.5; (*Z*)-2-chloro-1-phenylpropene, 24.2; propiophenone, 39; (*E*)-1-acetoxy-1-phenylpropene, 45; (*Z*)-1-acetoxy-1-phenylpropene, 51. To check for isomerization, a 0.85:1 mixture of (*E*)- to (*Z*)-2-chloro-1-phenylpropene (0.06 *M*) was allowed to react in 0.75 *M* HCl containing 0.34 *M* TMAC for 28 hr at 50°; analysis by glpc showed that the ratio of isomers was unchanged.

Results

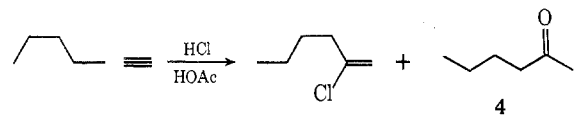
Phenylacetylene. The reaction of phenylacetylene with HCl in HOAc at 25° was found to yield two products, α-chlorostyrene (**1**) and acetophenone (**2**). Quantitative



1 **2**

measurements at 1–10% conversion showed that the product composition does not vary with time, indicating that secondary reactions of the initial products are unimportant under these conditions. Initial rates and product compositions for reaction in the presence and absence of tetramethylammonium chloride (TMAC) are given in Table I. The reaction yields primarily **1**, but the presence of 0.2 *M* TMAC, while causing a slightly greater than twofold increase in rate, results in a decrease in the ratio of **1** to **2**.

1-Hexyne. The reaction of 1-hexyne with HCl in HOAc was studied in a similar manner. At low conversion only two main products were observed. These were isolated using preparative glpc and their structures were established as 2-chloro-1-hexene (**3**) and 2-hexanone (**4**) on the

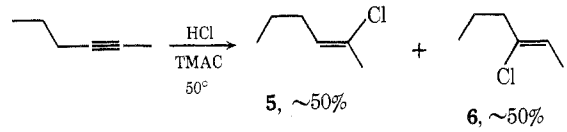


3 **4**

basis of their pmr spectra. At longer reaction times two additional products were observed by glpc. Moreover, the pmr spectrum of the peak corresponding to **3** changed, showing that a third new product with identical glpc retention time with that of **3** was being formed. These three products are observable only after significant (>1%) conversion of 1-hexyne to **3** has occurred and must, therefore, be secondary reaction products.

The structures of the secondary products were established using glpc-purified samples obtained from runs carried out to high conversion. One of the two glpc separable products proved identical in glpc retention time and pmr spectrum with authentic 2,2-dichlorohexane. The other had a pmr spectrum very similar to that of the secondary product having identical retention time with that of **3**; both pmr spectra were consistent with the structure 2-chloro-2-hexene and these two secondary products are therefore assigned as the isomeric 2-chloro-2-hexenes.

In order to confirm this assignment and establish the stereochemistry of the 2-chloro-2-hexenes, 2-hexyne was treated with HCl in HOAc containing TMAC. By analogy with the results obtained with 3-hexyne[2] this reaction was expected to yield a mixture of (*Z*)-2-chloro-2-hexene (**5**) and (*Z*)-3-chloro-2-hexene (**6**). At 78% conversion three



5, ~50% **6**, ~50%

product peaks were observed by glpc, one accounting for 97% of the product and having a retention time identical with that of **3** and the unidentified 2-chloro-2-hexene isomer obtained from 1-hexyne. The pmr spectrum of the glpc-purified material showed that it was composed of essentially equal amounts of **5** and **6**. Thus, the 2-chloro-2-hexene obtained from 1-hexyne which has the same retention time as **3** is **5** and the one with different retention time must be (*E*)-2-chloro-2-hexene (**7**).

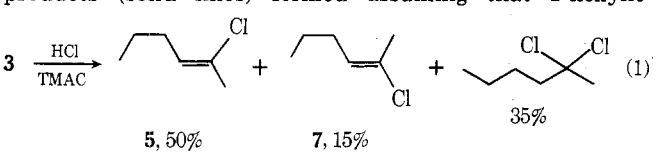
A quantitative study of the 1-hexyne reaction in the presence of TMAC showed that, once formed, **3** reacts with HCl to give the three secondary products in the approximate amounts shown in eq 1. Figure 1 shows the results of glpc analysis of the reaction products at less than

Table II
Effect of TMAC on the Hydrochlorination of 1-Phenylpropyne in Acetic Acid

[HCl], *M*	[C_9H_8], *M*	[TMAC], *M*	10^2 *R*,[a] *M* sec^{-1}	Product composition, %[b] 10	11	12[c]	14
			0.0°				
0.75	0.80	0.209	24	49	40	7.5	4.1
			25.0°				
0.10	0.10	0	1.1	81	8	11	≤0.3
0.10	0.10	0.080	2.2	59	26	10	4.2
0.10	0.10	0.16	3.2	51	34	8	6.4
0.10	0.10	0.50	5.7	36	46	7	10.6
0.75	0.10	0	26	80	12	8	0.3
0.75	0.10	0.063	34	62	24	11	≤3.2
0.75	0.10	0.167	67	53	33	9	5.5
0.75	0.10	0.50	94	39	45	8	8.4
0.75	0.10	1.00	102	30	51	10	10
0.75	0.80	0	198	77	12	11	0.1
0.75	0.80	0.094	318	59	28	11	2.2
0.75	0.80	0.188	411	52	34	11	3.4
0.75	0.80	0.209	470	51	35	10	3.8
			50.0°				
0.75	0.80	0	2,080	77	12	11	≤0.3
0.75	0.80	0.209	5,580	53	33	10	3.4
			80.0°				
0.75	0.80	0	23,400	74	13	13	≤0.3

[a] Average deviation less than ±5%. [b] In all cases, **13** constituted <0.3% of the products. [c] Includes small amounts of HOAc adducts; *cf.* ref 1.

10% conversion. Also shown are the calculated amounts of products (solid lines) formed assuming that 1-hexyne

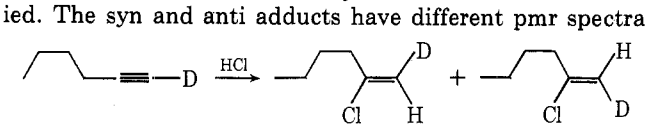


5, 50% **7**, 15%

undergoes a pseudo-first-order reaction to give **3** and **4** as the initial products in a ratio of 83.5:16.5 and that **3** undergoes a secondary reaction (eq 1) following pseudo-first-order kinetics at a rate equal to that of 1-hexyne. The reaction was simulated on a programmable electronic calculator to obtain the calculated product distribution as a function of time. The agreement between calculated and observed values shows that the assumptions concerning the primary product composition, and the rate and products for secondary reaction of **3**, are valid.

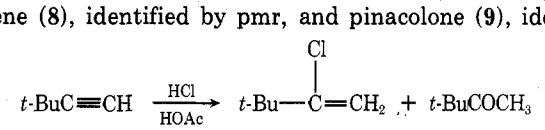
Values for the initial rate and the product composition for addition of HCl to 1-hexyne in the presence and absence of TMAC are given in Table I. The important features of these results are (1) in the absence of TMAC substantially more ketone than choride is formed; (2) TMAC causes a marked increase in reaction rate which is reflected primarily in increased chloride formation.

In order to establish the stereochemistry of addition to 1-hexyne, the reaction of 1-hexyne-*1-d* with HCl was studied. The syn and anti adducts have different pmr spectra



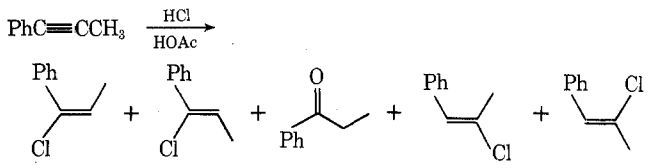
in benzene solution, the proton cis to the alkyl group being shifted to higher field and having a large coupling to the C-3 methylene group relative to the proton trans to the alkyl group.[9-11] Reactions were run at 50°, rather than 25°, so that reasonable amounts of product (25–50% conversion) could be obtained in a period of 2–3 weeks. The peak corresponding to **3** was isolated by preparative glpc and the stereochemistry was established from the relative areas of the two vinylic resonances in the pmr spectrum measured in benzene. For reaction of 1-hexyne-*1-d* (0.8 *M*) with 0.75 *M* HCl, the ratio of anti to syn adduct was found to be 40:60, whereas in the same reaction conducted with 0.2 *M* TMAC present the ratio was 90:10. These results establish that TMAC accelerates the reaction primarily by promoting the anti addition of HCl.

***tert*-Butylacetylene.** A study of addition to *tert*-butylacetylene (3,3-dimethyl-1-butyne) showed that >94% of the product at <10% conversion is 2-chloro-3,3-dimethyl-1-butene (**8**), identified by pmr, and pinacolone (**9**), identified by comparison to an authentic sample. Initial rates and product ratios determined at <3% conversion are given in Table I. As with 1-hexyne, less chloride than ketone is formed in the absence of TMAC, and the presence of TMAC increases the amount of chloride formed with an accompanying increase in reaction rate.



8 **9**

1-Phenylpropyne. The reaction of 1-phenylpropyne with HCl in HOAc was studied at <10% conversion using methods described in an earlier report.[1] The major products in the absence of chloride salts include the HCl adducts (*E*)- and (*Z*)-1-chloro-1-phenylpropene, and propiophenone as the secondary product formed from the HOAc adducts as initial products.[1] The HCl adducts from proton attack at C-1, (*E*)- and (*Z*)-2-chloro-1-phenylpropene, each account for <0.3% of the product in the absence of chloride salts. However, in the presence of TMAC, significant amounts of **14** (but not **13**) are observed. In a control experiment, it was shown that **13** is stable to the reaction conditions so that **14** is not formed by secondary isomerization of **13**.



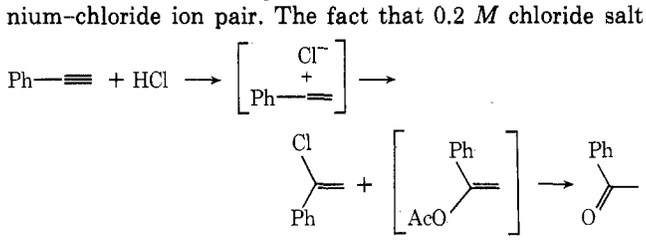
10 **11** **12** **13** **14**

The results of quantitative studies of the reaction under various conditions are given in Table II. The most impor-

tant feature of the results is that the presence of TMAC in the reaction mixture leads to a marked increase in the amount of 11 formed and causes 14 to become an important reaction product.

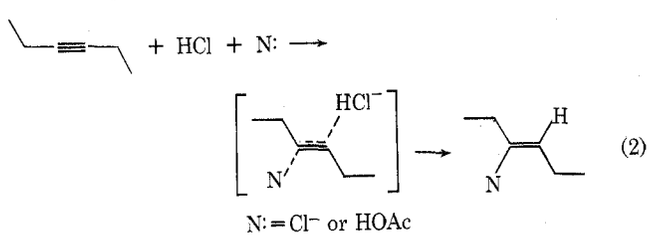
Discussion

Addition to Phenylacetylene. The results obtained show that phenylacetylene reacts exclusively *via* the AdE2 mechanism. The high ratio of chloride to ketone (12:1) is consistent with that expected from a collapse of a carbonium–chloride ion pair. The fact that 0.2 *M* chloride salt



increases the reaction rate by a factor of only 2 and does not increase the fraction of chloride formed (Table I) implicates the AdE2 process. In fact, the presence of 0.2 *M* chloride salt actually results in a decrease in the ratio of chloride to ketone to 7:1. A similar observation was made in the analogous reaction of styrene.[3] Since capture by added nucleophile is a long-standing criterion for establishing the presence of a carbonium ion intermediate, this seems, at first, a surprising observation. However, it must be remembered that the species formed in the present reaction is a tight ion pair and very probably collapses within the solvent cage without ever encountering external nucleophile. The effect of added salt in reducing the fraction of chloride formed can then be reasonably explained as a medium effect which slightly weakens the ion-pair interaction and thereby increases capture by solvent.

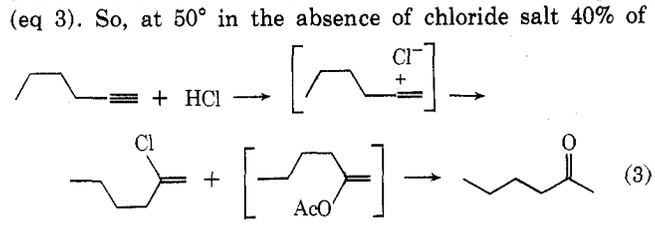
Addition to 1-Hexyne. The results obtained with 1-hexyne are quite different, and resemble those observed previously with 3-hexyne (Table I).[2] Specifically, the low ratio (0.54) of chloride to ketone in the absence of chloride salt, the increase in this ratio with added chloride salt, and the nearly eightfold rate increase caused by 0.2 *M* TMAC are indicative of chloride ion catalysis and reaction primarily *via* competing Ad3 addition of HCl and HOAc (eq 2). Yet, the stereochemical results indicate that



(2)

N: = Cl^- or HOAc

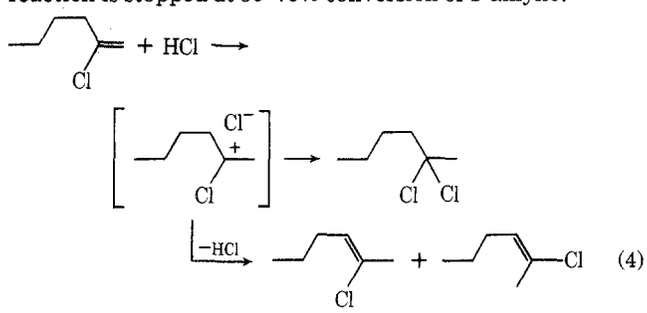
a fraction of the reaction does occur *via* an AdE2 path (eq 3). So, at 50° in the absence of chloride salt 40% of



(3)

the 2-chloro-1-hexene is formed by syn addition. Since the carbonium chloride ion pair favors collapse to syn adduct, the AdE2 mechanism is implicated. Assuming that a comparable fraction of syn adduct obtains at 25° and that no more than an equal amount of ketone derives from the AdE2 process, about 35% of the reaction at 0.8 *M* HCl could occur *via* the vinyl cation, with 15 and 50% occurring *via* Ad3 addition of HCl and HOAc, respectively. On the same basis 95% of the reaction involves *anti* Ad3 addition of HCl when 0.2 *M* TMAC is present.

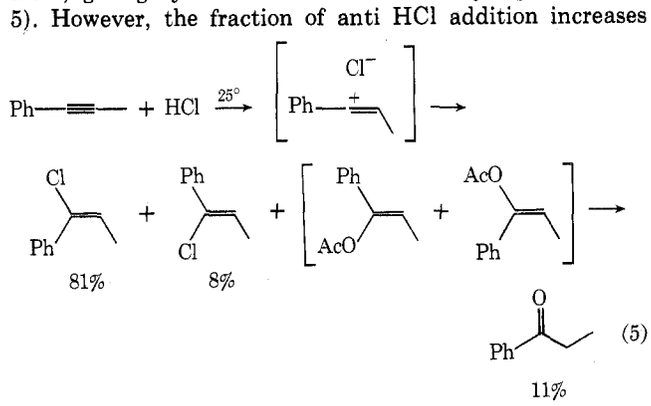
A fairly complete product study was made with 1-hexyne and the results illustrate the complexities that can arise as the result of secondary reactions of the initial products. Thus, 1-chloro-1-hexene is about as reactive as 1-hexyne itself and gives rise to products consistent with an AdE2 reaction of 2-chloro-1-hexene with HCl (eq 4). Reasonable yields of 2-chloro-1-alkenes are obtained from 1-alkynes only at high chloride ion concentration and when the reaction is stopped at 50–75% conversion of 1-alkyne.



(4)

Addition to *tert*-Butylethylene. Since it had been found previously that *tert*-butylethylene reacts with HCl in HOAc *via* an AdE2 mechanism in which Wagner–Meerwein rearrangement accounts for ~40% of the product,[3] it was of some interest to ascertain whether *tert*-butylacetylene would react similarly. However, the substantial effect of chloride salt upon the reaction rate and the ratio of chloride to ketone (Table I) show that reaction of *tert*-butylacetylene occurs primarily *via* competing Ad3 addition of HCl and HOAc rather than *via* the AdE2 mechanism. This conclusion is consistent with the fact that little or no rearrangement accompanies the addition. This observation shows that Ad3 addition is favored, relative to AdE2 addition, to a greater extent for alkynes than for the corresponding alkenes. It is clear, however, that *tert*-butylacetylene can react *via* an AdE2 mechanism involving a cationic intermediate under other reaction conditions. Thus, Griesbaum and Rehman[12] find for reaction of HCl with *tert*-butylacetylene in the absence of solvent that 30–60% of the product derives from an intermediate in which a methyl group has shifted from C-3 to C-2.

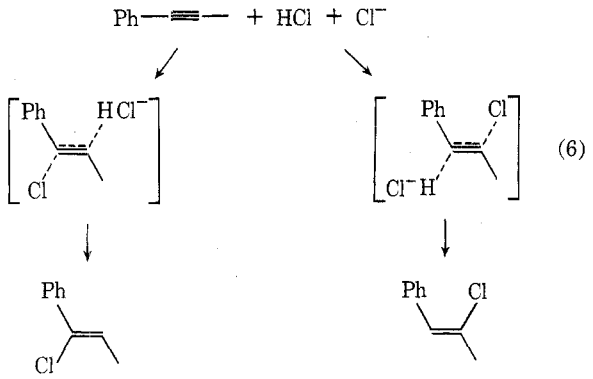
Addition to 1-Phenylpropyne. At low HCl concentration and in the absence of chloride salt addition to 1-phenylpropyne occurs predominantly by the AdE2 mechanism, giving syn HCl adduct as the major product (eq 5). However, the fraction of anti HCl addition increases



(5)

markedly in the presence of chloride salt and a new product appears which arises from anti HCl addition with proton attack at C-1 rather than C-2. At >0.5 *M* chloride salt these two products together account for over half of the total. In view of the fact that chloride salt does not in-

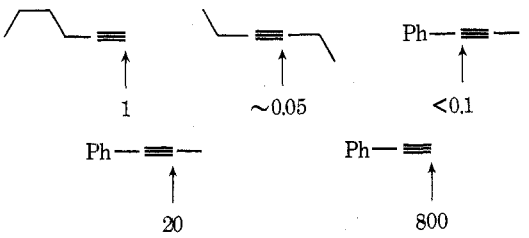
crease the fraction of chloride formed in the reaction of phenylacetylene, where a vinyl cation of similar stability is formed, this observation with 1-phenylpropyne cannot plausibly be attributed to capture of an intermediate vinyl cation by the added chloride salt. These products logically derive from competing anti Ad3 reactions as shown in eq 6.



(6)

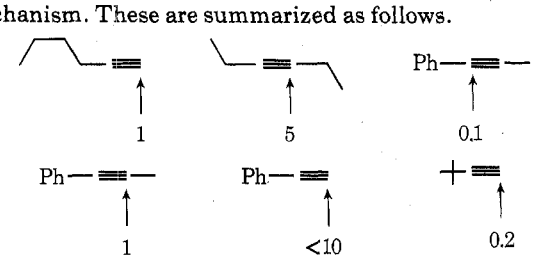
The results with 1-phenylpropyne demonstrate an important difference in the regiospecificity, as well as in stereospecificity, of the AdE2 and Ad3 additions. Thus, while addition *via* the AdE2 mechanism occurs with proton attack at C-2 occurring at least 300 times more rapidly than attack at C-1, the corresponding ratio for attack in the Ad3 mechanism is only about five.

Relative Reactivity in AdE2 Addition. From the results obtained in the absence of chloride salts and the foregoing analysis it is possible to assign relative rates for reaction *via* the AdE2 mechanism. The results are summarized below, arrows indicating the position of proton attack. The value for 3-hexyne[2] has been reduced by the

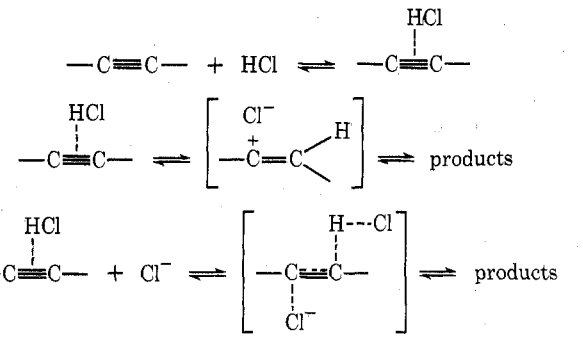


statistical factor of 2. The relative rates vary by a factor of $\sim 10^4$ and we see that substitution of alkyl by phenyl at the incipient cationic carbon results in a rate increase of between 400 and 800. This clearly reflects the ability of the phenyl group to stabilize the intermediate vinyl cation. Replacement of H by alkyl at the position of proton attack results in a rate decrease of between 20-fold and 40-fold. This effect is of the same magnitude as found for hydration of 1-phenylpropyne relative to phenylacetylene[13] and has been attributed to a larger change in C–C than in C–H bond energies as the hybridization of carbon varies from sp to sp^2 upon formation of the vinyl cation.[13]

Relative Reactivity in Ad3 Addition. Using the initial rate data obtained in the presence of 0.2 *M* chloride salt and the mechanistic assignments described above, relative rates were calculated for addition of HCl *via* the Ad3 mechanism. These are summarized as follows.



Scheme I



The relative rates span a range of less than 10^2. We see that substitution of alkyl by phenyl at the site of chloride attachment results in a decrease in rate, in sharp contrast to the large increase found for AdE2 addition. This shows that the Ad3 transition state does not closely resemble a vinyl cation intermediate.

The Ad3 transition state does not appear to be strongly subject to steric effects. The observation that Ad3 addition to 2-hexyne gives essentially equal amounts of anti HCl adduct from attack at C-2 and at C-3 shows that *n*-Pr and Me exhibit no differentiating effect. The comparison of 1-hexyne with *tert*-butylacetylene above shows that even the *t*-Bu group causes only a fivefold reduction in rate.

Comparing 1-hexyne and 3-hexyne we see that replacement of H by alkyl at the site of proton attack results in a modest rate increase for addition *via* the Ad3 mechanism, the effect again being opposite to that found for AdE2 addition. This observation indicates that the transition state for Ad3 addition involves little rehybridization at the site of proton attack.

Reaction Mechanism. These differences in reactivity support the view that the AdE2 and Ad3 mechanism involve distinctly different transition states. The transition state for AdE2 addition must closely resemble the vinyl cation chloride ion pair intermediate. The transition state for Ad3 addition is described as having little cationic character and little rehybridization at the carbon attacked by the proton. These considerations are summarized in Scheme I.

An acetylene–HCl molecular complex is formulated here as a common intermediate to obviate the implication of a termolecular collision in the Ad3 process. There is no direct evidence for involvement of such a complex and association of the reactants within a solvent cage would serve the same purpose. However, the description of the Ad3 transition state as a distorted acetylene–HCl complex associated with chloride ion accommodates the available structure–reactivity data.

The same general scheme applies for reaction of olefins with HCl in HOAc, and some qualitative comparisons of olefin and acetylene reactivity are possible. Both styrene[3] and phenylacetylene react exclusively *via* the AdE2 mechanism with styrene being about threefold more reactive than phenylacetylene under similar conditions. Judging from the rates of syn HCl addition, AdE2 addition to cyclohexene[4,5] is about tenfold faster than AdE2 addition to 3-hexyne.[2] These differences are similar to those found for addition of trifluororoacetic acid addition to alkenes and alkynes.[10,14] The anti Ad3 addition of HCl occurs at about the same rate for cyclohexene and 3-hexyne, and is the dominant reaction in both cases. Reaction of *tert*-butylethylene occurs about fivefold more rapidly than that of *tert*-butylacetylene but the evidence indicates that an AdE2 mechanism operates for the olefin and an Ad3

mechanism for the acetylene. This change in mechanism may arise from the somewhat greater reactivity of olefins than acetylenes *via* the AdE2 mechanism, possibly combined with a lower sensitivity to steric effects for Ad3 addition to acetylenes relative to olefins. For both olefins and acetylenes the balance between AdE2 and Ad3 addition appears to be delicate, so that changes in reactant structure or reaction conditions can lead to a shift from one mechanism to the other as the predominant pathway for reaction.

Acknowledgments. This work was supported by National Science Foundation Grant GP 24562. We thank Mr. Raymond Carrillo for technical assistance with some of the experiments, and Professor Paul E. Peterson for helpful comments.

Registry No.—**3,** 10124-73-9; **5,** 42131-99-7; **7,** 42132-01-4; 2,2-dichlorohexane, 42131-89-5; 1-hexyne-*1-d,* 7299-48-1; 2-hexyne, 764-35-2; (*E*)-3-chloro-2-hexene, 4050-45-7; 1-phenylpropyne, 673-32-5.

References and Notes

(1) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **88**, 5555 (1966).
(2) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **90**, 2124 (1968).
(3) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **91**, 3865 (1969).
(4) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Amer. Chem. Soc.*, **92**, 2810 (1970).
(5) R. C. Fahey and M. W. Monahan, *J. Amer. Chem. Soc.*, **92**, 2816 (1970).
(6) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **93**, 2445 (1971).
(7) R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965).
(8) C. DuFraisse and J. E. Viel, *Bull. Soc. Chim. Fr.*, **37**, 877 (1925).
(9) E. B. Whipple, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **82**, 3010 (1960).
(10) P. E. Peterson, R. J. Bopp, and M. Ajo, *J. Amer. Chem. Soc.*, **92**, 2834 (1970); R. J. Bopp, Ph.D. Thesis, St. Louis University, St. Louis, Mo., 1967.
(11) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).
(12) K. Griesbaum and Z. Rehman, *J. Amer. Chem. Soc.*, **92**, 1417 (1970).
(13) D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Amer. Chem. Soc.*, **87**, 2295 (1965); D. S. Noyce and M. D. Schiavelli, *J. Org. Chem.*, **33**, 845 (1968).
(14) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Amer. Chem. Soc.*, **87**, 5163 (1965).

Acid-Catalyzed Hydrolysis of Monoalkyl Xanthates[1]

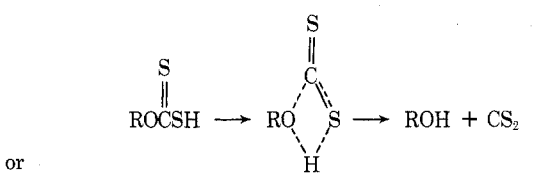
Clifford A. Bunton,* Patricia Ng, and Luis Sepulveda

Department of Chemistry, University of California, Santa Barbara, California 93106, and Faculty of Chemical Sciences, University of Chile, Santiago, Chile

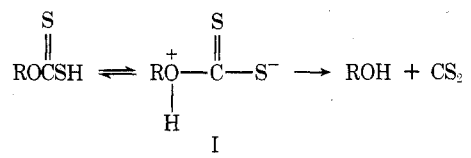
Received October 5, 1973

The decomposition of *n*-butyl xanthate in water, pH <5, and in metanolic methanesulfonic acid gives *n*-butyl alcohol and CS_2 by spontaneous elimination from xanthic acid. Similar observations were made on ethyl xanthate in water. At pH <0 the rate decreases because of the formation of unreactive protonated xanthic acid, and acid dissociation constants for both protonation equilibria are calculated. The decomposition of *tert*-butyl xanthate occurs with alkyl–oxygen fission and isobutylene is a major product. The reaction is much faster than that of *n*-butyl xanthate, and the rate is proportional to the concentration of *tert*-butylxanthic acid up to 1 *M* HCl or $HClO_4$, but at higher hydrogen ion concentrations protonation of *tert*-butylxanthic acid increases the rate. The activation parameters for reaction of *n*-butyl- and *tert*-butylxanthic acid are, respectively, $\Delta H^* = 16.3$ and 18.1 kcal mol^{-1}, and $\Delta S^* = -8.4$ and 2 eu.

Monoalkyl xanthates and their derivatives are important in the cellulose industry and in mineral flotation.[2] The acid-catalyzed hydrolyses of ethyl xanthate have been examined by several workers,[4,5] and at pH >2 the first-order rate constant was proportional to the concentration of ethylxanthic acid. It has been suggested that an ion-pair complex of a proton and an alkyl xanthate ion is the reactive species,[6] but such an ion pair seems to be an improbable reactive intermediate and alternative formulations of a unimolecular mechanism are



or



I

Similar spontaneous unimolecular eliminations have been observed in decarboxylations[7] and hydrolysis of phosphate ester monoanions.[8] However, the evidence does not exclude the $A_{Ac}2$ mechanism of ether hydrolysis.[9]

The rate of hydrolysis of ethylxanthic acid reaches a maximum at *ca.* 0.5 *M* HCl and then decreases. This behavior was treated in terms of formation of a xanthic acid–hydronium ion association,[5] but Iwasaki and Cooke detected a new species spectrophotometrically when the acid concentration was >0.5 *M*, and they suggested that this was the unreactive protonated xanthic acid.[4b] However, similar rate maxima are very common in the acid hydrolysis of weakly basic substrates such as amides, and are explained, at least partially, in terms of decreasing water activity at acidities where the substrate is fully protonated.[10] Rate maxima are also observed in A2 hydrolyses of some weakly basic substrates, such as aryl phosphates[8] and phosphonates.[11] However, these reactions involve nucleophilic attack by water. In the hope of throwing more light on this problem, we used *n*-butyl and *tert*-butyl xanthate, because the ease of formation of the *tert*-butyl cation might introduce a new mechanism of hydrolysis,[12] with a change in the dependence of rate upon acidity. A few experiments were also made with ethyl xanthate.

Experimental Section

Materials. The potassium alkyl xanthates were prepared in the usual way by the reaction of CS_2 with the alkoxide ion in the alcohol or CS_2 as solvent.[13] They were purified by precipitation from the alcohol or acetone by addition of Et_2O followed by recrystallization.