The Rates of Ionisation of 1 : 1-*Dimethylprop*-2-*ynyl Chloride and its* 3-*Alkyl Derivatives, and the Nature of the Baker–Nathan Effect.*

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The rates of solvolysis and of alkaline hydrolysis of 1 : 1-dimethylprop-2-ynyl chloride (3-chloro-3-methylbut-1-yne) and its 3-alkyl derivatives $CR\vdots C\cdot CMe_2Cl$ in 80% ethanol and their hydrolysis in wet formic acid are determined. They proceed by the unimolecular mechanism, except for the bimolecular alkaline hydrolysis of 1 : 1-dimethylprop-2-ynyl chloride itself and possibly for its ethanolysis. The introduction of a 3-alkyl group produces 1000-fold acceleration of ionisation, establishing the ability of the $C{\equiv}C$ bond to transmit polar effects strongly. The rates of the unimolecular reactions in 80% ethanol decrease in the order 3-Me > Et > Pr^i > $Bu^t \gg$ H, *i.e.*, the Baker–Nathan effect is observed. This effect is attributed to the steric inhibition of bond contraction and the resulting reduction of stabilisation of the R–C bonds increasing in the order Me ⟶ CMe_3 in the carbonium ions formed. Only inductive electron displacements are involved.

Normally the electron-donating power of alkyl groups increases in the order (H <) Me < Et < Pr^i < Bu^t. However, an (apparent) reversal of this order is often observed in chemical equilibria and reactions. This was first noted by Baker and Nathan (*J.*, 1935, **1844**) in the study of the kinetics of the bimolecular combination of 4-substituted benzyl bromides with pyridine.

This effect has always been observed in the unimolecular hydrolysis of substituted alkyl halides, in which ionisation is the rate-determining step. The results are summarised in Table 1. In the case of the bromides $R\cdot CH_2Br$ in moist formic acid there is some contribution from the bimolecular reaction, which is predominant with methyl bromide itself. The effect of alkyl groups in the corresponding tertiary chlorides appears to be irregular, but this has been attributed by Brown and Fletcher and by Brown and Stern (see footnotes to Table 1) to the contribution from an additional factor, namely, the relief by ionisation of the steric strain present in the original halide. In its absence, the Baker–Nathan effect would be more prominent, in particular, $Bu^t\cdot CMe_2Cl$ would ionise more slowly.

Table 1. *Rates of unimolecular hydrolyses of alkyl halides.**

Series	Solvent	Temp.	H	Me	Et	Pr^i	Bu^t
$R\cdot CH_2Br$ [1]	$H\cdot CO_2H$	95°	0·0174	0·027	0·0185	—	0·0153
$R\cdot CMe_2Cl$ [2]	80% EtOH	25	0·000019 †	0·092	0·153	0·081	0·111
$H_2C\colon CH\cdot CHRCl$ [3] ...	$H\cdot CO_2H$	44·6	0·000036 ‡	2·05	—	—	0·91
$RHC\colon CH\cdot CH_2Cl$ [3] ...	$H\cdot CO_2H$	44·6	0·000036 ‡	1·283	—	—	0·817
p-$RC_6H_4\cdot CH_2Br$ [4] ...	$H\cdot CO_2H$	25·1	0·00368	0·213	—	—	0·103
p-$RC_6H_4\cdot CHPhCl$ [5]...	80% $COMe_2$	25	0·728	15·6	12·6	10·04	7·96

* Values are given as 10^4k_1 (sec.$^{-1}$).

† Estimated by Cooper and Hughes from experiments at higher temperatures (*J.*, 1937, **1184**).

‡ Estimated by Vernon from experiments at higher temperatures (*loc. cit.*).

[1] Dostrovsky and Hughes, *J.*, 1946, 171. [2] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1949, **71**, 1845; Brown and Stern, *ibid.*, 1950, **72**, 5068; Shorter and Hinshelwood, *J.*, 1949, 2412. [3] Vernon, *J.*, 1954, 423. This paper appeared after completion of the present investigation. [4] Bevan, Hughes, and Ingold, *Nature*, 1953, **171**, 301. [5] Hughes, Ingold, and Taher, *J.*, 1940, 949.

We considered it possible that a knowledge of the unimolecular solvolysis of compounds containing the various alkyl groups attached to triple bonds would throw light on the Baker–Nathan effect and the effect of alkyl groups in general, and have investigated conductimetrically the kinetics of the solvolysis of 1 : 1-dimethylprop-2-ynyl chloride and its 3-alkyl derivatives $CR\vdots C\cdot CMe_2Cl$, where R = H, Me, Et, Pr^i, and Bu^t, in 80% aqueous ethanol, in the absence and in the presence of sodium hydroxide. Results are summarised in Table 2.

The solvolysis of 3-chloro-3-methylbut-1-yne is very slow at 25°. The initial rates could be measured accurately and follow the kinetics of a first-order irreversible reaction (k_1, 8·43 × 10^{-4} hr.$^{-1}$). After 100 hr. (8% reaction) the velocity coefficient decreases, probably owing to irreversible side reactions in which hydrogen chloride is consumed. Favorskaya (*J. Gen. Chem., U.S.S.R.*, 1939, **9**, 386, 1237) and Hennion, Sheehan, and Maloney (*J. Amer. Chem. Soc.*, 1950, **72**, 3542) have shown that, in the presence of

TABLE 2. *Kinetic data for the solvolyses and alkaline hydrolyses of the compounds* $\mathrm{CR{:}C{\cdot}CMe_2Cl}$ *in* 80% *ethanol.*

Reaction Temp.	10^4k_1, Alk. hydr. 25°	10^4k_1, Solv. 25°	10^4k_1, Solv. 25°	10^4k_1, Solv. 15°	$10^{12}B$, Solv.	E, Solv.
R = H	(7·1) *	0·00237	0·00234	—	—	—
Me	4·9	5·13	5·10	1·48	1·7	21·2
Et	4·6	4·90	4·90	1·415	1·7	21·2
Pr^i	3·45	3·42	3·41	0·934	5·8	22·1
Bu^t	2·77	2·80	2·78	0·768	4·1	22·0

k_1 and B are the first-order velocity constant and Arrhenius frequency factor in sec.$^{-1}$, respectively. E is the Arrhenius activation energy in kcal./mole. * Second-order velocity constant.

concentrated hydrochloric acid, isomerisation to 1-chloro-3-methylbuta-1 : 2-diene, $\mathrm{CHCl{:}C{:}CMe_2}$, and 2-chloro-3-methylbuta-1 : 3-diene, $\mathrm{CH_2{:}CCl{\cdot}CMe{:}CH_2}$, takes place. We have confirmed that isomerisation also occurs in our experiments. After the reaction mixture had been heated at 80° (in a stoppered flask) for 9 hr. to complete the reaction, the total content of ionised and labile chloride dropped to 81·5% of its original value, indicating approximately 18% isomerisation.

The alkaline hydrolysis of 3-chloro-3-methylbut-1-yne in 80% ethanol is much faster and follows the kinetics of a second-order irreversible reaction (k_2, 7·1 × 10^{-4} l. mole^{-1} sec.$^{-1}$). It occurs by a bimolecular mechanism. The products of this reaction were not examined, but the results of previous investigations of nucleophilic reactions of this and similar compounds have shown that normal nucleophilic substitution (S_N2), substitution with rearrangement (S_N2'), and elimination ($E2$) occur simultaneously, though in a varying degree (cf. Zakharova, *J. Gen. Chem., U.S.S.R.*, 1947, **17**, 688; Pudovik, *ibid.*, 1951, **21**, 1462, 1811).

Our determinations do not allow a decision whether the solvolysis (in absence of alkali) occurs by the unimolecular or by the bimolecular mechanism, or whether both mechanisms occur simultaneously. Pudovik (*loc. cit.*) measured the rates of solvolysis of this substance in 50% ethanol and in 40% acetone at 35° (k_1, 0·132 and 0·08 hr.$^{-1}$, respectively) and, in spite of the absence of conclusive evidence, suggested that the solvolysis is unimolecular.

A comparison with data available for other compounds suggests that the bimolecular reaction could make an appreciable contribution. Thus, the ratio k_2/k_1, where k_2 and k_1 are the velocity constants for the alkaline hydrolysis and solvolysis in 80% ethanol respectively, is 3000 : 1 in the case of 3-chloro-3-methylbut-1-yne. For methyl and ethyl bromide, which are known to undergo solvolysis by the bimolecular mechanism, the corresponding ratios are of the same order (6000 : 1 and 1250 : 1, respectively).

The rates of solvolysis in 80% ethanol of the 3-alkyl-1 : 1-dimethylprop-2-ynyl chlorides ($\mathrm{RC{:}C{\cdot}CMe_2Cl}$; where R is Me, Et, Pr^i, and Bu^t) measured at 25° (in duplicate) and at 15° are much faster and not affected by the presence of alkali. The rate-determining step in these reactions is thus the ionisation of the alkyl chloride.

The solvolyses follow the kinetics of first-order irreversible reactions up to about 60—75% of reaction. Beyond that point allowance must be made for the reversibility of solvolysis and, possibly, of the ionisation itself. The equilibrium positions corresponded to approximately 92—98% of reaction, but except with the *tert.*-butyl derivative they could not always be determined exactly because the reversible hydrolyses are accompanied by slower irreversible reactions (such as hydrogen chloride elimination). Hence, the velocity coefficients for the final stages of the reactions are in some cases slightly unreliable. However, we have established that no hydrogen chloride is consumed in irreversible reactions such as the formation of isomeric chlorides or addition to the triple bond. The velocity coefficients for the solvolyses in presence of sodium hydroxide at 25°, calculated for first-order irreversible reaction, are reasonably constant and almost identical with those found in absence of alkali.

The rates of unimolecular solvolysis of the compounds $CR\vdots C\cdot CMe_2Cl$ increase in the order $H \ll Bu^t < Pr^i < Et < Me$. Table 2 also shows the Arrhenius activation energies and frequency factors for solvolysis (except for the parent substance, the mechanism of solvolysis of which is uncertain). The activation energies tend to increase from the methyl to the *tert.*-butyl derivative, but too much significance cannot be attached to the numerical values obtained since the Arrhenius activation energy is known to be not quite representative of the true activation energy (corresponding to the potential-energy difference). The inadequacy of the Arrhenius equation probably explains also the variation in the frequency factor B, which is roughly parallel to the smaller variation in E (cf. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, 184 *et seq.*; Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford Univ. Press, 1947, 266 *et seq.*).

The hydrolysis in formic acid containing small amounts of water has also been investigated, the rates being followed by the titration methods developed by Bateman and Hughes (*J.*, 1937, 1187; 1940, 940, 945). The velocity coefficients for 3-chloro-3-methylbut-1-yne at 25°, calculated for a first-order reversible reaction, were found to be independent of the concentration of water (0·4 and 0·5% respectively), showing that ionisation of the molecule is the rate-determining step. However, the reaction is not free from complications causing a decrease of the calculated velocity coefficients with time. This is due to consumption of hydrogen chloride in irreversible reactions, as shown by a decrease in time of the total labile and ionised chloride content (cf. comments on the solvolysis in 80% ethanol) and possibly to irreversible elimination which is followed by addition of water to the elimination product (cf. Rupe and Kambli, *Helv. Chim. Acta*, 1926, **9**, 672; Hennion, Davis, and Maloney, *J. Amer. Chem. Soc.*, 1949, **71**, 2813).

These kinetic complications were eliminated by the addition of an excess of calcium formate to the reaction mixture to remove the free hydrogen chloride as liberated. The reaction is still unimolecular, in spite of the possibility of some nucleophilic action by the formate ion (cf. Bateman and Hughes, *loc. cit.*), since the velocity coefficients calculated for a first-order reversible reaction are constant (at 15°; k_1, $2{\cdot}7 \times 10^{-2}$ hr.$^{-1}$).

The 3-alkyl homologues were also hydrolysed under the same conditions, but the rapidity of their hydrolysis and the very considerable experimental error involved did not allow the determination of velocity constants of sufficient accuracy to measure their small differences. Their hydrolysis is approximately 5000 times faster than that of the parent hydrogen compound.

Originally, a few experiments were carried out with prop-2-ynyl bromide in wet formic acid at 75°, but no free hydrogen bromide had been liberated after 3 hr. Addition of hydrogen bromide to the triple bond is quite rapid at this temperature but hydrolysis is very slow. This is similar to the findings of Hatch and Chiola (*J. Amer. Chem. Soc.*, 1951, **73**, 361), who attempted to measure the rates of hydrolysis of prop-2-ynyl chloride and its 3-methyl homologue in aqueous hydrochloric acid, in the presence and in the absence of cuprous chloride, and observed the addition of hydrogen chloride to the triple bond. The investigation of this series of halides appeared unpromising and was discontinued in favour of that of the tertiary halides discussed.

DISCUSSION

The effect of solvation being ignored, the rate of ionisation of an alkylhalide will depend on two factors: (1) The energy of heterolytic fission of the C–Hal bond resulting in the formation of a cation (or a transition state) possessing linkages identical with those in the original undissociated molecule: this will decrease with the increasing electron-donating character of the substituents in the original molecule. (2) The energy of stabilisation of (all the individual linkages in) the cation (or transition state) formed: this is generally assumed to increase with the electron-donating inductomeric or electromeric electron displacements.

The Nature of the Baker–Nathan Effect.—This effect as observed in the unimolecular hydrolysis (ionisation) of the 3-alkyl-1 : 1-dimethylprop-2-ynyl chlorides (Table 2) and of other series of alkyl halides (Table 1) is generally attributed to hyperconjugation; *i.e.*, idealised structures involving H^+, such as $H^+\ H_2C{:}C{:}C{:}CH_2$ in the case of 3-alkyl-1 : 1-dimethylprop-2-ynyl chlorides, are assumed to contribute strongly to the stability of the cations. It is, therefore, noteworthy that in the series $R\cdot CMe_2X$, $R\cdot CH{:}CH_2X$, $H_2C{:}CH\cdot CHRX$, and $RC\vdots C\cdot CMe_2X$ the rates of ionisation of the *tert.*-butyl derivatives ($R = Bu^t$) are a few thousand times greater than those of the corresponding parent substances ($R = H$), although hyperconjugation involving structures containing H^+ is not possible, and that, in contrast, the increase on replacement of a methyl group in *tert.*-butyl by a hydrogen atom is only very small (about 25%).

This very considerable effect of the *tert.*-butyl group can be attributed to an inductive effect within the undissociated alkyl halide causing a reduction of the energy of heterolytic fission of the C–Hal bond (1) and to an increased stabilisation of the cation involving an inductive electron displacement (2). In this case, each of the three substituting methyl groups in *tert.*-butyl can only be responsible for less than one-sixth of the total inductive effect of this group. Thus, hyperconjugation involving one C–H bond, if it exists, could also contribute only a similar amount to the total electronic effect, although it could be expected to be more pronounced in the carbonium ions than in any other known system. It would be of the same order of magnitude as the inductive effect of the substituting methyl groups, irrespective of whether the alkyl groups are attached to a double bond, a triple bond, or directly to the C atom acquiring a positive charge. This interpretation requires the replacement of one appreciable electronic effect by an alternative one of the same magnitude, in order to account for some small differences.

This view also implies that the hyperconjugative electron displacement increases more strongly than the inductive one as the electron-demand increases. Thus, in simple neutral molecules such as propene and propyne, in which hyperconjugation has been claimed to be the main factor responsible for the shortened C–C bond distances and increased C–C bond energies (Pauling, Springall, and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 927; Mulliken, *J. Chem Phys.*, 1939, **7**, 339; Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41), it could only make a much smaller contribution than in the carbonium ions. The observed effects scarcely necessitate this hypothesis. This is supported by a consideration of the energetics of hyperconjugation. The energy differences between structures such as $H^+\ H_2C{:}CH\cdot\bar{C}H_2$ and $H^+\ H_2C{:}C{:}\bar{C}H$ and the corresponding conventional structures $H_3C\cdot CH{:}CH_2$ and $H_3C\cdot C\vdots CH$ respectively are not less than 370 kcal., since they involve at least the ionisation of a hydrogen atom (312 kcal.) and the homolytic fission of a C–H bond (100 kcal.). Even in the 3-methylprop-2-ynyl cation the difference in energy between $H_3C\cdot C\vdots C\cdot\overset{+}{C}H_2$ and $H^+\ H_2C{:}C{:}C{:}CH_2$ is at least 130 kcal.

Alternatively, the considerable effect of the *tert.*-butyl group could be attributed to a contribution from hyperconjugated structures involving $\overset{+}{C}H_3$ instead of H^+ such as $H_3\overset{+}{C}\ CMe_2{:}C{:}C{:}CMe_2$ (cf. Berliner and Bondhus, *J. Amer Chem. Soc.*, 1948, **70**, 854; Vernon, *loc. cit.*). This view would be able to account for the Baker–Nathan effect if one assumes that hyperconjugation involving H^+ structures would make only a slightly greater contribution than that involving $\overset{+}{C}H_3$ structures (and some smaller contribution from the inductive effect), that both types of hyperconjugation would make similar, but now possibly the main contributions to the stability of the cations, and that somehow the H^+ hyperconjugation would increase more strongly than $\overset{+}{C}H_3$ hyperconjugation with increasing electron demand. It should, therefore, be noted that the energy required to form a proton is about 100 kcal. greater than that required to form a methyl cation, since the bond energy of the C–C linkage (80 kcal.) is about 20 kcal. less than that of C–H, and the ionisation potential of the hydrogen atom (312 kcal.) exceeds that of the methyl radical (231 kcal.;

cf. Price, *loc. cit.*) by about 80 kcal. Thus, Me^+ hyperconjugation, if existing, should be more important than that involving H^+, which would be at variance with the factual requirements.

What is possibly even more important, the hypothesis of hyperconjugation cannot explain why the Baker–Nathan effect is observed in the basicities of the aliphatic amines $R\cdot NH_2$ (Table 3), for which hyperconjugated structures cannot be formulated, and why it is not observed in the ionisation potentials of the alkylbenzenes (Table 3), although they involve the formation of molecule ions.

TABLE 3.

Property	Compound	R = H	Me	Et	Pr^i	Bu^t
p*K*	$R\cdot NH_2$ [1]	9·27	10·64	10·67	10·63	10·45
I.P. (ev)	$R\cdot C_6H_5$ [2]	9·24	8·92	8·75	8·6	8·5

[1] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1930, **52**, 5115; 1932, **54**, 3469. [2] Price, *Chem. Reviews*, 1947, **41**, 257.

It has already been shown (Burawoy, *Trans. Faraday Soc.*, 1944, **40**, 537; *Chem. and Ind.*, 1944, **51**, 434; "Contribution à l'Étude de la Structure Moléculaire," Desoer, Liége, 1947/48, p. 73) that the valency conception of non-localised bonds, which forms also the basis of the hypothesis of hyperconjugation, is in disagreement with numerous observations and is not required to explain the constitutive changes of covalent linkages. They can be accounted for less ambiguously and more consistently by a consideration of inductive electron displacements only which originate in changes of the effective nuclear charges at individual atoms (their screening). An increase of the positive charge at the C atom of a linkage C–X will be responsible for a "stereomeric" effect, *i.e.*, an attraction of the electrons shared with X accompanied by a shortening and strengthening of the bond. The magnitude of the changes will depend on the polarisability of the electronic system of X and on the increasing repulsive interaction between the nuclei and between the inner orbit electrons respectively of C and X resisting bond contraction and stabilisation. The steric repulsions between the groupings attached to C and those attached to X will also play a part (for a more detailed discussion illustrated by examples, see Burawoy, *loc. cit.*).

This view leads to an interpretation of the Baker–Nathan effect which is similar to one already suggested for the apparent inversion of the normal polar effect of the halogen atoms sometimes observed in chemical changes (Burawoy, 1947/48, *loc. cit.*). Thus, the polarity of the C–Hal bond in the original alkyl halide molecule $R\cdot CH_2\cdot Hal$ will increase and its energy of heterolytic fission will be reduced in the order of the increasing electron-donating inductive effect of the alkyl groups R (factor 1). On the other hand, in the cations $R{-}\overset{+}{C}H_2$ formed (or the transition state obtained during ionisation) the contraction and stabilisation of the $R{-}C^+$ bond will be reduced by the steric repulsions increasing with the size of the alkyl groups R (factor 2). The magnitude of the stabilisation energy (and its reduction due to the steric inhibition of bond contraction) will increase as the effective nuclear charge at the C^+ atom increases. Factor 1 will facilitate ionisation in the order $Me < Et < Pr^i < Bu^t$, factor 2 in the reverse order. In the ionisation of the alkyl halides, the latter factor is more important and, therefore, a Baker–Nathan effect is observed.

This interpretation is free from the inconsistencies resulting from the introduction of hyperconjugation. It is strongly supported by the fact that the Baker–Nathan effect is encountered only in chemical equilibria and other changes in which bond stabilisations and bond contractions within one of the two entities involved play an important part, and that it is not observed in physical properties such as dipole moments, ionisation potentials (cf. below), and, as will be shown elsewhere, electronic spectra, which do not involve bond contractions.

It explains the Baker–Nathan effect observed in the basicities of the aliphatic amines $R\cdot NH_2$. In this case the effect is less pronounced, because the increase of the effective nuclear charge at the N atom in the ammonium ions $R\cdot\overset{+}{N}H_3$, which determines the stabilisation energy, will be due to the addition of a proton and will be smaller than that at the charged C atom in the carbonium ions due to a removal of an electron pair.

The decrease of the ionisation potentials of alkylbenzenes in the order of substituents $\mathrm{Me} > \mathrm{Et} > \mathrm{Pr^i} > \mathrm{Bu^t}$ is also accounted for. The ionisation potentials derived from spectroscopic data depend on the inductive electron-donating effect of the alkyl groups, *i.e.*, the polarisability of the electronic system. They do not involve changes of interatomic distances in the molecule ion formed and, thus, are not affected by any steric inhibition of bond contraction which is responsible for the Baker–Nathan effect.

The Effect of 3-*Alkyl Groups.*—The acceleration of ionisation of the investigated 3-alkyl-1 : 1-dimethylprop-2-ynyl chlorides as well as of the 3-alkylallyl chlorides discussed by Vernon (*loc. cit.*) on replacement of a $C_{(3)}$-hydrogen atom by an alkyl group is of the same magnitude as that caused by the introduction of an alkyl group in the 1-position (cf. Table 1). This shows that a triple bond (like a double bond) strongly transmits the stereomeric effect, *i.e.*, the increased effective nuclear charge, from the 1- to the 3-position. One might have expected that the effect of the alkyl groups would decrease with their distance from the C–Hal bond and the charged atom in the cation respectively, but this may be balanced by the greater electron-donating character of alkyl groups when attached to multiple linkages. The smaller rate increase due to alkyl groups substituted in the *para*-position of a phenyl group may be due to the former factor.

The Effect of the Ethynyl Group.—Bartlett and Rosen (*J. Amer. Chem. Soc.*, 1942, **64**, 543) and Hatch and Chiola (*loc. cit.*) found that primary prop-2-ynyl halides react with potassium iodide 50—100 times as fast as do the corresponding saturated halides; *i.e.*, the replacement of hydrogen by an ethynyl group produces an acceleration of nucleophilic substitution by the bimolecular mechanism. Comparing the ethynyl with the ethyl group, Zakharova and Dobromyslova (*J. Gen. Chem.*, *U.S.S.R.*, 1950, **20**, 2029) pointed out that the electron-attracting effect of the ethynyl group should facilitate attack by a nucleophilic reagent, but hinder ionisation. This is true, but our experiments show that the ionisation of 1 : 1-dimethylprop-2-ynyl chloride in 80% ethanol at 25° is approximately 100 times faster than that of *iso*propyl chloride (cf. Table 1), *i.e.*, the replacement of *hydrogen* by an ethynyl group facilitates ionisation. This establishes that the expected appreciable increase of the energy of heterolytic fission of the C–Cl bond due to the electron withdrawal by the ethynyl group is counterbalanced by an even greater increase in the energy of stabilisation of the carbonium ion (or transition state) resulting mainly from the polarisation and contraction of the $C_{C\equiv C}{-}C^+$ bond.

EXPERIMENTAL

Preparations.—1 : 1-Dimethylprop-2-ynyl chloride and its homologues were prepared by the general route: acetylene → acetylenic alcohol → acetylenic chloride. All acetylenic alcohols and chlorides were purified by alternate fractional distillation under reduced pressure and fractional crystallisation. Most of the m. p.s have not been recorded previously.

2-*Methylbut*-3-*yn*-2-*ol.*—This alcohol was prepared by the action of acetone on sodium acetylide in liquid ammonia (Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882); it had b. p. 104°/760 mm., m. p. 2° (Campbell and Eby, *ibid.*, 1941, **63**, 2683, give 2°).

3-*Chloro*-3-*methylbut*-1-*yne.*—The chloride was prepared by treatment of 2-methylbut-3-yn-2-ol with concentrated hydrochloric acid (Hennion, Sheehan, and Maloney, *loc. cit.*); it had b. p. 75°/760 mm., m. p. —61° (Found: Cl, 34·3. Calc. for C_5H_7Cl: Cl, 34·6%).

2-*Methylpent*-3-*yn*-2-*ol.*—This alcohol is not obtainable in appreciable yields by the action of acetone on sodium methylacetylide in either liquid ammonia or ether. It was prepared by the action of acetone on prop-1-ynylmagnesium bromide (Hurd and Cohen, *ibid.*, 1931, **53**, 1068; Zakharova, *J. Gen. Chem.*, *U.S.S.R.*, 1947, **17**, 688); the acetylenic Grignard compound was obtained by passing methylacetylene (15% excess) into ethereal ethylmagnesium bromide at −25°; it had b. p. 80°/100 mm., 134°/760 mm., m. p. −13·5°, d_4^{20} 0·8763 (Found: C, 73·3; H, 10·0. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%).

4-*Chloro*-4-*methylpent*-2-*yne.*—Into a mixture of pure 2-methylpent-3-yn-2-ol (68·5 g.), light petroleum (b. p. <40°, 200 c.c.), finely powdered calcium chloride (20 g.), and quinol (1 g.)

dry hydrogen chloride was passed for 4 hr. with vigorous stirring, at 0°. The light petroleum layer was decanted, shaken with anhydrous potassium carbonate, and dried ($MgSO_4$). After removal of the solvent and fractionation of the residue, 4-chloro-4-methylpent-2-yne (51 g., 62·5%) had b. p. 63°/100 mm., m. p. $-5{\cdot}1°$, d_4^{25} 0·9247 (Found: C, 62·2; H, 7·4; Cl, 29·6. Calc. for C_6H_9Cl: C, 61·8; H, 7·8; Cl, 30·4%). Hurd and Cohen (*loc. cit.*) and Zakharova (*loc. cit.*) claimed to have prepared 2-methylpent-3-yn-2-ol and 4-chloro-4-methylpent-2-yne, but the former authors obtained an alcohol boiling at 75—77°/15 mm. and yielding a chloride of b. p. 57—61°/47 mm., and the latter an alcohol and chloride boiling at 80°/100 mm. and 60°/100 mm., respectively. Our products are identical with those obtained by Zakharova. Moreover, in physical properties they resemble the other members of the series so strongly as to leave no doubt as to their identities.

2-*Methylhex*-3-*yn*-2-*ol*.—This alcohol was obtained by the action of acetone on but-1-ynylmagnesium bromide (cf. Dupont, *Compt. rend.*, 1909, **148**, 1524; Picon, *ibid.*, 1914, **158**, 1184); b. p. 75°/60 mm., 144°/760 mm., m. p. −6° (Found: C, 74·4; H, 10·5. Calc. for $C_7H_{12}O$: C, 74·9; H, 10·8%).

2-*Chloro*-2-*methylhex*-3-*yne*.—Pure 2-methylhex-3-yn-2-ol (80 g.), dissolved in light petroleum (b. p. <40°; 200 c.c.), was treated with dry hydrogen chloride in presence of powdered calcium chloride (24 g.) and quinol (1 g.). 2-*Chloro*-2-*methylhex*-3-*yne* was worked up like 4-chloro-4-methylpent-2-yne; it (62·4 g., 67%) had b. p. 76°/100 mm., m. p. −62°, d_4^{25} 0·9035 (Found: C, 64·1; H, 8·7; Cl, 27·0. $C_7H_{11}Cl$ requires C, 64·4; H, 8·5; Cl, 27·1%).

2 : 5-*Dimethylhex*-3-*yn*-2-*ol*.—To a solution of ethylmagnesium bromide [obtained from magnesium (54 g.), ethyl bromide (132 g.), and dry ether (720 c.c.)] 3-methylbut-1-yne (84 g.) dissolved in dry ether (125 c.c.) was added dropwise (1 hr.) with mechanical stirring and ice-cooling. After 24 hr. pure acetone (70 g.) was added dropwise, and the mixture set aside for 24 hr., refluxed finally for 30 min., and poured on ice (2000 g.) and 1 : 1 hydrochloric acid (400 c.c.). The product was extracted with ether. After being dried (K_2CO_3) and subsequent removal of the ether, 2 : 5-*dimethylhex*-3-*yn*-2-*ol* was fractionated; the alcohol (98·5 g., 65%) had b. p. 148°/760 mm., m. p. −6·5°, d_4^{20} 0·8438 (Found: C, 75·8; H, 11·1. $C_8H_{14}O$ requires C, 76·1; H, 11·2%).

2-*Chloro*-2 : 5-*dimethylhex*-3-*yne*.—This compound was obtained by the action of dry hydrogen chloride on 2 : 5-dimethylhex-3-yn-2-ol (50 g.) in light petroleum (60 c.c.) in the presence of calcium chloride (15 g.) and quinol (0·5 g.), by the procedure used for 4-chloro-4-methylpent-2-yne; the *chloride* (34·5 g., 60%) had b. p. 79°/100 mm., m. p. −48°, d_4^{25} 0·8790 (Found: C, 66·0; H, 8·8; Cl, 24·2. $C_8H_{13}Cl$ requires C, 66·4; H, 9·1; Cl, 24·5%).

2 : 5 : 5-*Trimethylhex*-3-*yn*-2-*ol*.—This alcohol, prepared according to Hennion and Bannigan (*J. Amer. Chem. Soc.*, 1946, **68**, 1202), had b. p. 150°/760 mm., m. p. 32° (Hennion and Bannigan give 32°).

5-*Chloro*-2 : 2 : 5-*trimethylhex*-3-*yne*.—This chloride, prepared according to Hennion and Bannigan (*loc. cit.*), had b. p. 81°/100 mm., m. p. 17° (Hennion and Bannigan give 15°) (Found: Cl, 22·1. Calc. for $C_9H_{15}Cl$: Cl, 22·3%).

Rate Determinations.—Solvolyses in 80% *aqueous ethanol.* About 1 ml. of freshly purified halide was added to about 100 ml. of solvent (both at the required temperature), giving solutions M/12—M/20 with respect to alkyl halide. The same solvent (ethanol : water = 4 : 1 by vol.) was used for all solvolyses. The solvent used for the alkaline hydrolyses (ethanol : water : N-NaOH = 8 : 1 : 1) was made up freshly before each determination. The thermostatic control was accurate to ±0·01°.

The amount of hydrogen chloride liberated after various reaction times was determined conductimetrically. The conductivity bridge employed had a discrimination of at least 1 part in 1000. For each set of experimental conditions a calibration chart was prepared showing conductivity against amount of hydrogen chloride added, the relation being not quite linear. The resistance of the platinum electrode cell was checked before each rate determination. An allowance was made for the change in the conductivity of the solvent (by about 1%) due to the addition of about 1% (by volume) of alkyl halide.

In solvolysis the amount of hydrogen chloride liberated was measured directly, no other electrolyte being present, and a high degree of accuracy and reproducibility could be attained. The data for the alkaline solvolysis (hydrolysis) are less accurate since the conversion of sodium hydroxide into sodium chloride is accompanied by a much smaller change in conductivity. Moreover, the electrode was slightly less reliable in alkaline solution. In solvolysis the total amount of chloride present (ionised and labile organic) was estimated by titration of a sample of the reaction mixture by Volhard's method. In alkaline hydrolyses, which are irreversible, the amount of chloride present initially was taken to be identical with the total hydrogen chloride liberated after completion of the reaction.

The results are illustrated by a few characteristic examples. Except for the alkaline hydrolysis of 4-chloro-4-methylpent-2-yne, only half the data available are reproduced, but the mean velocity coefficient is calculated from all measurements, some of the less reliable initial values (given in parentheses) being ignored.

Alkaline hydrolysis of $\text{CH}{\equiv}\text{C}\cdot\text{CMe}_2\text{Cl}$ *at* 25°.

Init. [RCl] = 4·84 ml. of 1N.

t (hr.)	0·5	0·75	1·0	2·0	3·0	3·5	4·0	5·0	6·0	16·1	∞
HCl (ml. of 1N)	0·53	0·80	1·03	1·8	2·35	2·6	2·8	3·2	3·45	4·52	4·84
k_2 (l. mole^{-1} hr.$^{-1}$)	(2·33)	2·49	2·48	2·54	2·52	2·55	2·55	2·65	2·63	2·50	—

k_2 (mean) = 2·56 l. mole^{-1} hr.$^{-1}$.

Solvolysis of $\text{CH}{\equiv}\text{C}\cdot\text{CMe}_2\text{Cl}$ *at* 25°.

Init. [RCl] = 8·88 ml. of 1N.

t (hr.)	7	10	23	25	30	35	47·1	50	102·2	150
HCl (ml. of 1N)	0·053	0·075	0·172	0·186	0·224	0·259	0·344	0·365	0·73	1·044
10^4k_1 (hr.$^{-1}$)	8·51	8·38	8·51	8·48	8·51	8·45	8·39	8·39	8·39	(8·33)

k_1 (mean) = 8·43 × 10^{-4} hr.$^{-1}$ (duplicate determination, 8·53 × 10^{-4}).

$\text{CMe}{\equiv}\text{C}\cdot\text{CMe}_2\text{Cl}$ at 25°						$\text{Me}_3\text{C}\cdot\text{C}{\equiv}\text{CMe}_2\text{Cl}$ at 25°					
Alkaline hydrolysis Init. [RCl] = 3·9 ml. of 1N			*Solvolysis* Init. [RCl] = 7·3 ml. of 1N			*Alkaline hydrolysis* Init. [RCl] = 5·5 ml. of 1N			*Solvolysis* Init. [RCl] = 5·13 ml. of 1N		
t (sec.)	HCl (ml. 1N)	10^4k_1 (sec.$^{-1}$)	t (sec.)	HCl (ml. 1N)	10^4k_1 (sec.$^{-1}$)	t (sec.)	HCl (ml. 1N)	10^4k_1 (sec.$^{-1}$)	t (sec.)	HCl (ml. 1N)	10^4k_1 (sec.$^{-1}$)
450	0·7	4·40	223	0·77	(5·01)	600	1·0	3·35	291	0·39	(2·71)
600	0·95	4·65	317	1·08	5·05	750	1·15	3·13	403	0·53	2·73
750	1·17	4·75	396	1·35	5·16	900	1·3	3·00	638	0·83	2·78
900	1·4	4·95	524	1·73	5·16	1200	1·6	2·87	982	1·24	2·82
1200	1·7	4·77	766	2·35	5·07	1500	1·9	2·83	1295	1·57	2·82
1500	2·05	4·97	936	2·75	5·05	1800	2·15	2·75	1752	1·98	2·78
1800	2·3	4·95	1198	3·35	5·13	2700	2·82	2·67	2100	2·25	2·75
2700	2·9	5·05	1500	3·87	5·04	3600	3·4	2·67	2700	2·71	2·78
3600	3·3	5·20	1800	4·39	5·11	4200	3·7	2·63	3000	2·88	2·75
7200	3·8	5·08	2100	4·60	5·12	4800	3·93	2·61	3600	3·25	2·74
∞	3·9	—	2400	5·15	5·09	6000	4·40	2·61	4800	3·75	2·78
			3000	5·69	5·13	7200	4·65	2·68	6000	4·11	2·77
			3600	6·07	5·09	10,800	5·1	2·60	10,800	4·77	2·78
			14,400	7·13 *	—	∞	5·5	—	28,800	4·98 *	—
k_1 (mean) = 4·9 × 10^{-4} sec.$^{-1}$.			k_1 (mean) = 5·1 × 10^{-4} sec.$^{-1}$.			k_1 (mean) = 2·77 × 10^{-4} sec.$^{-1}$.			k_1 (mean) = 2·78 × 10^{-4} sec.$^{-1}$.		

* Equilibrium.

Hydrolyses in Wet Formic Acid.—The experimental technique used to measure the comparatively slow hydrolysis of 1 : 1-dimethylprop-2-ynyl chloride was that employed by Bateman and Hughes for *tert.*-butyl chloride (*loc. cit.*). Samples were poured into carbon tetrachloride, which was extracted with water, and the halide content was estimated with silver nitrate.

Hydrolysis of $\text{CH}{\equiv}\text{C}\cdot\text{CMe}_2\text{Cl}$ *in formic acid at* 15°.

Init. [RCl] = 37·8 ml. of 0·01N; [H_2O] = 1%; [$\text{Ca(H}\cdot\text{CO}_2)_2$] = 0·6%.

t (hr.)	2	4·05	6	8	10	12	25	75	101
HCl (ml. of 0·01N)	2·3	3·9	5·4	7·2	8·4	10·3	18·5	33·3	35·6
10^2k_1 (hr.$^{-1}$)	(3·1)	2·7	2·5	2·6	2·5	2·7	2·7	2·8	2·8

k_1 (mean) = 2·7 × 10^{-2} hr.$^{-1}$ = 7·5 × 10^{-6} sec.$^{-1}$.

The alkyl derivatives of 1 : 1-dimethylprop-2-ynyl chloride are hydrolysed very rapidly under the same conditions, and some modification of the experimental method was necessary. The reaction was stopped by addition of a mixture of carbon tetrachloride and chloroform at −60°, the formic acid solidifying. Ice-water was added, and the mixture shaken. When all the material had liquefied the organic layer was separated without delay, and the hydrogen chloride in the aqueous layer was estimated as before. The results clearly show that further hydrolysis occurred during the extraction of the hydrochloric acid with water, causing the apparent velocity coefficient to be too high, especially after the shorter reaction times.

Hydrolysis of $\text{Me·C⋮C·CMe}_2\text{Cl}$ *in formic acid at* 15°.

Init. [RCl] = 36 ml. of 0·01N; $[H_2O]$ = 1%; $[Ca(H·CO_2)_2]$ = 0·6%.

t (sec.)	5	15	15	30	30	45	60
HCl (ml. of 0·01N)	12·7	22·7	22	29·9	28	31·5	33·6
10^2k_1 (sec.$^{-1}$)	8·7	6·6	6·3	5·9	5·0	4·6	4·4

k_1 (extrapolated) = ~ 4 × 10^{-2} sec.$^{-1}$.

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