Base-catalysed Hydrogen-exchange in Some Substituted [1-^{3}H]Acetylenes

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The rates of detritiation of X·C≡C·^{3}H compounds (X = ClCH$_2$, ICH$_2$, BrCH$_2$, Alkyl, PhCH$_2$, Ph, and Me$_3$Si) by buffered water–methanol (4:1 v/v) (pH *ca.* 8·05) have been measured at 25°. For the compounds with X = HalCH$_2$ or Alkyl, the effects of substituents correlate reasonably well with their Taft σ*-constants. The compounds PhC≡C^{3}H, and particularly, Me$_3$SiC≡C^{3}H are more reactive than would be expected from operation of inductive effects alone, and it is suggested that in these cases there is some conjugative withdrawal of electrons from the alkynyl group.

We have measured the rates of detritiation at 25° of some acetylenes, X·C≡C·^{3}H, in a mixture of methanol (1 vol.) and an aqueous buffer solution (pH 8·05 ± 0·02) (4 vol.). The results are shown in the Table as observed pseudo-first-order rate constants, *k*.

Rates of detritiation of X·C≡C·^{3}H compounds in buffered water–methanol (4 : 1 v/v; pH *ca.* 8·05) at 25°

X	10^4k (min.$^{-1}$)	X	10^4k (min.$^{-1}$)	X	10^4k (min.$^{-1}$)
Br·CH$_2$ ...	430	Me$_3$Si ...	66	n-C$_6$H$_{11}$ ...	9·4
Cl·CH$_2$ ...	390	Ph·CH$_2$ ...	25	Bu^t	8·9
I·CH$_2$	265	Pr^i	12·3	Neopentyl	7·0
Ph	250	Bu^n	9·7		

The Figure shows that a plot of —log$_{10}k$ against the Taft σ*-constants of the X groups[1] approximates to a straight line (ρ = 1·36). [A better straight line plot (ρ = 1·67) is obtained if a single value of zero is used for the σ*-constants of all the simple alkyl substituents, as suggested by Ritchie.[2]] This correlation with σ*-constants was expected, since there can be no direct steric influence of the substituent at the reaction site and since the effects of Y groups on detritiation of the compounds Y·C$_6$H$_4$·C≡C·^{3}H correlate well with their Hammett σ-constants.[3] Indeed, Kreevoy and his colleagues have observed a correlation with σ*-constants for hydrogen-exchange in four X·C≡C·H compounds in alkaline aqueous t-butyl alcohol, but the value of σ* was an experimentally derived quantity only for one of the substituents, and for the other three was calculated.[4]

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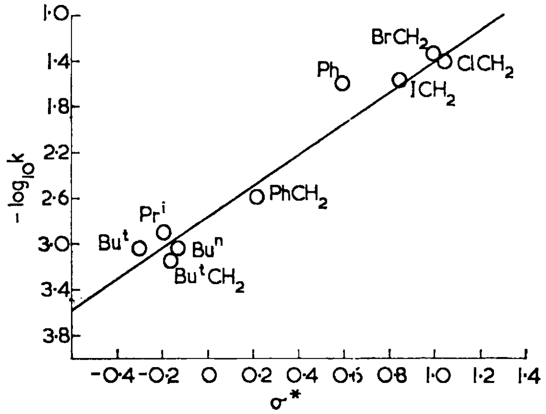
There are some features difficult to explain on simple qualitative reasoning if the absence of any steric effects is assumed. For example, the order of reactivity for the compounds with X = $ClCH_2$ and $BrCH_2$ is the opposite of that expected from inductive effects, as is that for the compounds with X = neopentyl and Bu^t. The differences are too small, however, to warrant detailed speculative consideration.

We think that the deviation from the line in the Figure of the point for X = Ph is real and significant (but see ref. 4), and arises from a conjugative interaction between the phenyl and the alkynyl group which can operate to withdraw electrons from the latter. This conjugation may possibly be enhanced in the transition state, which is thought to be close to the carbanion $X{\cdot}C{\equiv}C^-$,[4,5] for while there can, of course, be no direct delocalisation of the unpaired electron pair,[5] electrostatic repulsion between this electron pair and the π-electrons of the alkynyl bond might increase their overlap with the π-orbitals of the ring. Conjugative electron-withdrawal, involving interaction of the p_π-orbitals of the alkynyl group with the d-orbitals of the trimethylsilyl group, accounts for the high reactivity of the $Me_3SiC{\equiv}C^3H$ compound compared with that of the $Me_3CC{\equiv}C^3H$ compound; the operation of inductive effects alone would make the silicon-containing compound less reactive than its carbon analogue.[6]



EXPERIMENTAL

Preparation of Acetylenes.—Commercial samples of n-butyl-, n-hexyl-, and phenyl-acetylene were fractionated before use. t-Butyl-,[7] trimethylsilyl-,[8] neopentyl-,[9] and isopropyl-acetylene[10] were prepared by published methods. Benzylacetylene was prepared from 1,2,3-tribromopropene and phenylmagnesium bromide.[11] Propargyl bromide and chloride were prepared from propargyl alcohol and phosphorus tri-bromide or -chloride.[12]

Propargyl Iodide.—A mixture of propargyl chloride (30 g.), potassium iodide (100 g.), and AnalaR acetone (600 ml.) was refluxed for 72 hr., then added to crushed ice. Organic products were extracted with ether and worked up in the usual way.

Preparation of Tritiated Acetylenes, $X{\cdot}C{\equiv}C^3H$.—Tritiated propargyl halides were prepared by shaking a homogeneous mixture of the halide with a weakly alkaline mixture of tritiated water and alcoholic alkali (cf. ref. 3). Other acetylenes were tritiated by hydrolysing the alkynylmagnesium bromides with tritiated water (50 mc./ml.), followed by excess of ordinary water (cf. ref. 3). The physical properties of the tritiated phenyl-, t-butyl-, neopentyl-, and trimethylsilyl-acetylene used are listed elsewhere.[3,13] Those of other tritiated acetylenes were as follows: (X =) n-hexyl, b. p. 125°, n_D^{20} 1·4155 (cf. ref. 14); Bu^n, b. p. 66—67°, n_D^{20} 1·3982 (cf. ref. 15); Pr^i, b. p. 30°, n_D^{20} 1·3818 (cf. ref. 10); $BrCH_2$, b. p. 80—82°, n_D^{23} 1·4908 (cf. ref. 12); $ClCH_2$, b. p. 62° (cf. ref. 12); ICH_2, b. p. 58°/110 mm. (cf. ref. 12); $PhCH_2$, b. p. 55—58/5 mm., n_D^{20} 1·5500 (cf. ref. 11).

Rate Measurements.—The medium was identical with that used previously.[3] The method previously used for rate measurements was modified because of the volatility of some of the acetylenes used. Samples (1·5 ml.) of the aqueous methanolic buffer solution–tritiated acetylene mixture were sealed in glass ampoules which were placed in the thermostat bath at 25° ± 0·02°. The ampoules were withdrawn at suitable intervals and broken under a mixture of sulphuric acid and a toluene solution of the scintillator.[3]

With benzyl- and iodomethyl-acetylene, a substantial amount of activity remained after 10 half-lives, and this did not fall further, but good first-order plots were obtained up to more than 80% completion of the reaction. Presumably either inert tritiated impurity was present or some tritium had entered a non-acetylenic position during the tritiation.

We thank the S.R.C. for a Research Studentship (to G. A. S.), and the Royal Society and the Courtauld Educational Trust Fund for the loan of apparatus.

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[6/568 *Received, May 10th,* 1966]

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