Reactions in Strongly Basic Solutions. Part VI.[1] Correlation of the Rates of Rearrangement of Weak Carbon Acids in Aqueous Dimethyl Sulphoxide with an Acidity Function. Substituent and Kinetic Isotope Effects

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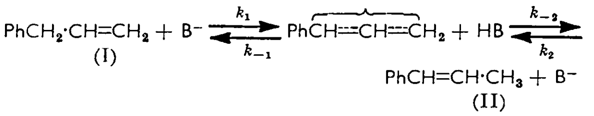
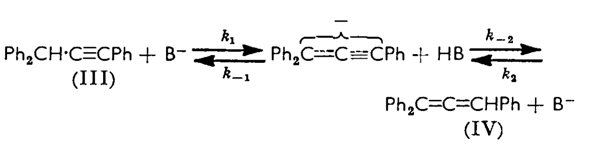
The rates of the base-catalysed isomerisation at 30·0 °C of a series of 3- and 4-substituted allylbenzenes, 1,3,3-triphenylprop-1-yne and [3-^{2}H]-1,3,3-triphenylprop-1-yne, have been measured in aqueous dimethyl sulphoxide containing tetramethylammonium hydroxide and give linear correlations with the acidity function, H_-, for the medium. The Hammett reaction constant, ρ, for the allylbenzene rearrangement (*ca.* 3·5), the kinetic isotope effect for the 1,3,3-triphenylprop-1-yne rearrangement (*ca.* 7), the slopes of the acidity-function correlations, and other related evidence indicate rate-determining steps involving proton abstraction by the base. Estimates of the pK_a values of the carbon acids under study are made.

THE base-catalysed isomerisation of weak carbon acids has been studied in some detail, particularly regarding the intramolecularity of the reaction.[2] The isomerisation of allylbenzene (I) to propenylbenzene (II) has been studied in both t-butyl alcohol and dimethyl sulphoxide containing t-butoxide anion,[3] and in dimethyl sulphoxide containing methylsulphinyl carbanion.[4] The reaction was considered to proceed *via* proton abstraction by the base to give an intermediate carbanion, which forms the product as shown in equation (1).[3] Similarly,



$$\underset{\text{(I)}}{\mathrm{PhCH_2{\cdot}CH{=}CH_2}} + \mathrm{B^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overbrace{\mathrm{PhCH{=\!=}CH{=\!=}CH_2}}^{-} + \mathrm{HB} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \underset{\text{(II)}}{\mathrm{PhCH{=}CH{\cdot}CH_3}} + \mathrm{B^-} \qquad (1)$$

1,3,3-triphenylprop-1-yne (III) undergoes a base-catalysed 1,3-proton transfer to form triphenylallene (IV) in t-butyl alcohol, methanol, and methanolic dimethyl sulphoxide.[5] Again proton abstraction is considered to lead to a delocalised carbanion, as shown in equation (2). Both these reactions show varying



$$\underset{\text{(III)}}{\mathrm{Ph_2CH{\cdot}C{\equiv}CPh}} + \mathrm{B^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overbrace{\mathrm{Ph_2C{=\!=}C{\equiv}CPh}}^{-} + \mathrm{HB} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \underset{\text{(IV)}}{\mathrm{Ph_2C{=}C{=}CHPh}} + \mathrm{B^-} \qquad (2)$$

degrees of intramolecularity depending on the nature of the solvent and base.

Correlations between the rates of base-catalysed reactions and acidity functions have been reported for a

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number of reactions.[6-18] Primary kinetic hydrogen isotope effects for proton-transfer reactions have been extensively studied from both the experimental and theoretical viewpoints.[19-21] Substituent effects on the ionisation equilibria of carbon acids have also received considerable attention.[22,23] In this study, the rates of isomerisation have been measured at 30·0 °C in aqueous dimethyl sulphoxide containing $1{\cdot}10 \times 10^{-2}$M-tetramethylammonium hydroxide for allylbenzene and a series of 3- and 4-substituted allylbenzenes, as well as for 1,3,3-triphenylprop-1-yne and [3-^{2}H]-1,3,3-triphenylprop-1-yne. Correlations of the rates with an acidity function and an analysis of substituent and kinetic isotope effects are presented and discussed in terms of the details of the reaction path.

EXPERIMENTAL

Materials.—Allylbenzene was dried over 5 Å molecular sieves. The 3- and 4-substituted allylbenzenes were prepared from the corresponding substituted bromobenzenes. The allylbenzenes were fractionally distilled under reduced pressure and their physical constants [24,25] are shown in Table 1. 1,3,3-Triphenylprop-1-yne was synthesised by the method of Wieland and Kloss [26] and, after three recrystallisations from light petroleum (b.p. 80—100 °C), had m.p. 78—79° C (lit.,[26] m.p. 79 °C). [3-^{2}H]-1,3,3-Triphenylprop-1-yne was prepared by the method of Cram *et al.*[5] and, after three recrystallisations from light petroleum (b.p. 80—100 °C), had m.p. 77—78·5 °C (lit.,[5] 78—79 °C). The ^{1}H n.m.r. spectrum of a sample in carbon tetrachloride gave no detectable α-hydrogen signal and indicated the compound to be >95% pure ^{2}H-isomer. Dioxan, deuterium oxide, dimethyl sulphoxide, tetramethylammonium hydroxide, and water were as described previously.[6,27,28]

TABLE 1

Physical constants of the substituted allylbenzenes

Substituent	B.p./°C at mmHg	Lit. b.p./°C at mmHg	Ref.
H	28—30/0·5	160—163/748	24
3-Cl	37—38/0·7	198—202/760	25
4-Cl	32—33/0·3$_5$	199—201/760	25
3-Me	29—30/0·4	180—183/760	25
3-OMe	44·5—45·5/0·5	213—216/760	25

Products.—Conversion of the allylbenzenes into the propenylbenzenes was found to be >99·9% in aqueous dimethyl sulphoxide containing tetramethylammonium hydroxide by g.l.c. estimation.[29] Triphenylallene, m.p. 76—78 °C (lit.,[5] m.p. 77—78° C), the product of the isomerisation of 1,3,3-triphenylprop-1-yne, was isolated from the reaction in aqueous dimethyl sulphoxide containing tetramethylammonium hydroxide. The u.v.–visible spectrum of the products in the medium closely matched the spectrums of the kinetic runs at the completion of the reaction for both rearrangements.

Kinetic Measurements.—The preparation and measurements of the reactions were carried out as described in Part II.[6] Propenylbenzenes, produced by the isomerisation of allylbenzenes, absorb strongly in the range 250—270 nm in aqueous dimethyl sulphoxide and the reactions were followed by monitoring the rise of the product absorption at 260 nm. Similarly, triphenylallene, produced by the isomerisation of 1,3,3-triphenylprop-1-yne, was monitored at 265 nm.

RESULTS

The reactions of the allylbenzenes and 1,3,3-triphenylprop-1-yne with hydroxide anion were confirmed to be overall of the second order, being first order in each species. This was verified by observing the effect on the reaction rate of changing the hydroxide anion concentration in dilute aqueous dimethyl sulphoxide, where H_- may be considered proportional to log [OH$^-$].[30] The tetramethylammonium hydroxide was always in large excess and the reactions approximated to first-order behaviour. No deviation from linearity in the plot of the logarithm of optical density against time was observed during three half-lives of the reactions. First-order rate coefficients, k_{obs}, for the isomerisations are shown in Tables 2 and 3. Where applicable the H_- acidity function is shown.[6,31] The rate coefficients were reproducible to ±3%. Solvent compositions were reproducible to ±0·2%.

Correlations of the reaction rates with the H_- acidity function were made as described previously.[6] Constants of equation (3) are in Table 4.

$$\log k_{\mathrm{obs}} = lH_- + c \qquad (3)$$

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TABLE 2

Rate coefficients for the isomerisation of carbon acids in aqueous dimethyl sulphoxide containing 1·10 × 10^{-2}M-tetramethylammonium hydroxide at 30·0 °C, together with the acidity functions

Allylbenzene

Mol % Me_2SO	73·5	78·9	84·7	91·2	95·4	
H_-	19·89	20·44	21·17	22·10	23·19	
$10^4k_{obs}/s^{-1}$	0·806	2·12	7·50	50·5	284	

1-Allyl-3-chlorobenzene

Mol % Me_2SO	50·0	56·6	64·4	73·5	84·7	91·2
H_-	17·46	18·14	18·93	19·89	21·17	22·10
$10^4k_{obs}/s^{-1}$	0·283	0·768	2·69	14·9	176	998

1-Allyl-4-chlorobenzene

Mol % Me_2SO	64·3	68·8	73·5	78·8	84·8	91·2
H_-	18·92	19·40	19·89	20·42	21·18	22·10
$10^4k_{obs}/s^{-1}$	1·08	2·44	5·82	17·1	62·9	356

1-Allyl-3-methylbenzene

Mol % Me_2SO	73·6	78·9	84·7	91·2	95·4$_5$	
H_-	19·90	20·44	21·17	22·10	23·20	
$10^4k_{obs}/s^{-1}$	0·608	1·59	6·13	40·3	225	

1-Allyl-3-methoxybenzene

Mol % Me_2SO	68·7	73·6	78·8	91·2	95·5	
H_-	19·39	19·90	20·42	22·10	23·21	
$10^4k_{obs}/s^{-1}$	0·553	1·24	3·19	78·7	518	

1,3,3-Triphenylprop-1-yne

Mol % Me_2SO	14·4	18·8	27·4	34·5$_5$	39·0	
H_-	13·78	14·32	15·26	15·96	16·39	
$10^4k_{obs}/s^{-1}$	3·21	6·16	32·4	125	288	

[3-^{2}H]-1,3,3-Triphenylprop-1-yne

Mol % Me_2SO	18·8$_5$	27·3	34·7	39·1		
H_-	14·33	15·26	15·98	16·41		
$10^4k_{obs}/s^{-1}$	0·754	4·22	18·6	41·1		

TABLE 3

Rate coefficients for the isomerisation of 1,3,3-triphenylprop-1-yne in aqueous dioxan containing 1·10 × 10^{-2}M-tetramethylammonium hydroxide at 30 °C

Mol % dioxan	12·3	16·2	24·0	30·7	35·1	45·3
$10^5k_{obs}/s^{-1}$	3·95	4·57	5·95	7·79	9·06	11·3 (25·0,* 1·42 †)

* With deuterium oxide. † With [3-^{2}H]-1,3,3-triphenylprop-1-yne.

TABLE 4

Regression analyses for equation (3) correlating the isomerisation of carbon acids in aqueous dimethyl sulphoxide containing 1·10 × 10^{-2}M-tetramethylammonium hydroxide and extrapolated rate coefficients in water at 30·0 °C *

	l	c	Correlation coefficient	log k_{obs} (water)
Allylbenzene	0·77	−19·43	0·999	−10·16
1-Allyl-3-chlorobenzene	0·77	−18·12	0·999	−8·85
1-Allyl-4-chlorobenzene	0·79	−19·02	1·000	−9·51
1-Allyl-3-methylbenzene	0·79	−19·99	0·999	−10·48
1-Allyl-3-methoxybenzene	0·79	−19·62	1·000	−10·11
1,3,3-Triphenylprop-1-yne	0·84	−15·32	1·000	−5·21
[3-^{2}H]-1,3,3-Triphenylprop-1-yne	0·84	−16·13	1·000	−6·02

* Aqueous 0·011M-Me_4NOH has $H_- = 12·04$.

DISCUSSION

Acidity Function–Rate Correlations.—The basis of linear relations between H_- and the logarithm of the observed first-order rate-coefficient have been discussed.[10,18,32] Reactions involving either rate-determining proton abstraction or a rapid pre-equilibrium formation of the anion followed by slow reaction may be correlated by use of equation (4), where HA and A^- represent the indicator acid and anion, RH is the kinetic substrate, and $f_\ddagger$ is the activity coefficient of the transition state. Equation (4) reduces to the general

$$\log k_{obs} = H_- + \log (f_{RH}f_{A^-}/f_{HA}f_\ddagger) + \text{constant} \qquad (4)$$

correlation equation (3) when $\log (f_{RH}f_{A^-}/f_{HA}f_\ddagger)$ is zero, constant, or a linear function of H_-. The use of equation (5), and related expressions containing the concentration of ' free water ', c_w, instead of a_w has been suggested.[10,32] As discussed in Part II,[6] deviations from linearity at high basicities for the plots against H_- and $H_- + \log a_w$

$$\log k_{obs} = H_- + \log a_w + \text{constant} \qquad (5)$$

for aqueous dimethyl sulphoxide are insufficient for this to be used as a mechanistic criterion. Thus the use of $H_- + \log a_w$ for the results of this study does not result in improved correlations, although the slopes obtained by use of equation (3) are somewhat less than those found by use of $H_- + \log a_w$.

The observed rate coefficient, k_{obs}, could be equal to either the ionisation step, k_1, or the product of the pre-equilibrium and collapse step to products, k_1k_{-2}/k_{-1}. Successful correlations such as those shown in Table 4 are not in themselves sufficient to distinguish between the two possibilities (*cf.* ref. 18). A knowledge of the collapse ratio,[2] k_{-1}/k_{-2}, or some other criterion is needed before such a distinction can be made. Cram *et al.* conclude that, from their studies of isomerisation and exchange, the slow rate-determining step for the rearrangement of allylbenzene and closely related substrates is the ionisation process [2,3] and imply the same for the rearrangement of 1,3,3-triphenylprop-1-yne.[5] While it is very likely that the same rate-determining step occurs in our study as those of Cram *et al.*,[3,5] it remains to be established.

The slopes, l, for the correlation of the isomerisation of the allylbenzenes and the two 1,3,3-triphenylprop-1-ynes at 30 °C are *ca.* 0·78 and 0·84, respectively. Correlations for the exchange of [α-^{3}H]acetophenone (pK_a = *ca.* 19) in several basic media at 25 °C have slopes in the range 0·3—0·5,[12] while those for the isotopic exchange of dimethyl sulphoxide (pK_a = 32 to 33) [11] in aqueous and alcoholic dimethyl sulphoxide at 25 °C have a slope of 0·93.[13] The slopes of similar correlations for the isotopic exchange and/or racemisation of several weak carbon acids (pK_a values from 22 to 33) [23] in methanol at 45 °C or methanolic dimethyl sulphoxide at 25 °C and 100—125 °C are in the range 0·8—1·0.[18] The relation between the slope, l, and the structure of the transition state for certain of these correlations has been discussed [12,13] and these slopes have been related to the extent of proton transfer in the transition state. This

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[32] C. H. Rochester, ' Acidity Functions,' Academic Press, London, 1970.

discussion, by analogy with the Hammond postulate,[33] suggests that the greater the difference in pK_a of the donor and acceptor the greater will be the slope when the transition state more closely resembles the products, with the transition state for the proton transfer process crudely represented by (V). The latter discussion very

$$\mathrm{R{-}H + OH^- \longrightarrow \underset{(V)}{[R^- \cdots H^+ \cdots OH^-]^{\ddagger}} \longrightarrow R^- + H_2O} \quad (6)$$

closely resembles the application of the Brønsted equation to base-catalysed reactions,[34] where the slope has been commonly related to degree to which the transition state resembles the products.[35] The application of this postulate to base-catalysed reactions of ' pseudo-bases ' has been strongly criticised.[36] The evidence concerning the base-catalysed reactions of weak carbon acids is as yet insufficient either to confirm or to refute the relation between the slope, *l*, and the structure of the transition state. As the carbon acids studied here have an acidity mainly resulting from their ability to delocalise the charge by resonance interactions to other carbon atoms, the likelihood that the postulate is sound remains. Therefore, the success of the correlations and the magnitude of the slopes found in this study could indicate that the transition states are very ' advanced,' resembling the carbanion products. This would be in accord with the large difference between the estimated pK_a values of the carbon acids under study here (see later Discussion) and the base employed as the catalyst.

Kinetic Solvent Isotope and Aqueous Dioxan Solvent Effects.—The effect of the variation of dioxan–water composition has been studied for the rearrangement of 1,3,3-triphenylprop-1-yne (Table 3). Our previous study [27] showed that an H_- scale could not be successfully generated in this medium. However, the comparatively large increase in rate with increasing dioxan content, compared with our previous studies,[27,28,37] indicates an ' advanced ' transition state requiring much less protic solvation that the initial state. The carbanion requires very little protic solvation [38] and destruction of the solvated hydroxide anion releases water. The observed kinetic solvent isotope effect, $k^{\mathrm{H_2O}}/k^{\mathrm{D_2O}}$, in 45·3 mol % dioxan–water at 30 °C can be calculated from the results in Table 3 as 0·45. Calculations, based on those of Bunton and Shiner,[39] can be made for models of the transition state, *i.e.*, (VI) the ' electrostatic ' model, (VII) the ' free-proton ' model (' electrostatic ' or ' free-proton ' model with $k^{\mathrm{H_2O}}/k^{\mathrm{D_2O}} =$ 0·78), and (VIII) the ' covalent ' model ($k^{\mathrm{H_2O}}/k^{\mathrm{D_2O}} =$ 0·43). These calculations are made relative to water,

$$\underset{\text{(VI)}}{\mathrm{R{-}H \cdots OH^-}} \qquad \underset{\text{(VII)}}{\mathrm{R^- \cdots H^+ \cdots OH^-}} \qquad \underset{\text{(VIII)}}{\mathrm{R^- \cdots HOH}}$$

but the effect of using aqueous dioxan appears to be small.[40] The results suggest that the transition state is comparatively ' advanced ' and more closely resembles (VIII) than (VI) or (VII). It should also be noted that the kinetic isotope effect, $k^{\mathrm{H}}/k^{\mathrm{D}}$ (see below), in aqueous dioxan (see Table 3) is with the range observed in aqueous dimethyl sulphoxide and the reaction mechanisms in the two media appear to be identical.

Kinetic Isotope Effect.—The studies of the isomerisation of 1,3,3-triphenylprop-1-yne and [3-^{2}H]-1,3,3-triphenylprop-1-yne enable the calculation of the kinetic isotope effect, $k^{\mathrm{H}}/k^{\mathrm{D}}$, at several H_- values. The values of $k^{\mathrm{H}}/k^{\mathrm{D}}$ are in the range 6·7—8·2 (with an uncertainty of ±0·5). While the magnitude of the kinetic isotope effect in this study clearly indicates that the ionisation step is rate-determining, the relation of this effect to the structure of the transition state is less certain. Bordwell and Boyle [20] have recently concluded either that $k^{\mathrm{H}}/k^{\mathrm{D}}$ is relatively insensitive to the symmetry of the transition state or that the symmetry does not change over wide ranges of ΔpK_a (ΔpK_a is the difference in pK_a between the substrate and the base), while a number of treatments [19,21] have related the extent of hydrogen transfer to the primary hydrogen isotope effect. However it seems that our results can only indicate that the transition state is ' advanced ' and comprises a developed carbanion. The extent of that development could range from approximately half-formed to an almost completely formed carbanion.

Hammett Reaction Constant.—Application of the Hammett equation (7) to the effects of *meta–para*-substitution in allylbenzene gives reaction constants,

$$\log (k/k^{\circ}) = \rho\sigma \qquad (7)$$

ρ, of 3·4 in 74·5 mol % dimethyl sulphoxide and 3·5 in 90·6 mol % dimethyl sulphoxide at 30 °C (see Table 5).

TABLE 5

Hammett correlations for the effects of *meta–para*-substitution in allylbenzene at 30 °C *

Solvent	ρ	*r*	*n*
74·5 Mol % Me_2SO	3·38	0·995	5
90·6 Mol % Me_2SO	3·54	0·995	5

* *r* Is the correlation coefficient and *n* the number of substituents.

Thus ρ appears to be almost constant over the range of dimethyl sulphoxide contents studied. A reaction constant of *ca.* 3·5 clearly confirms that the transition state has a high degree of carbanionic character. This closely compares with that of 3·2 for the exchange of 2-substituted 9-tritiofluorenes in methanolic methoxide at

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[40] A. R. Butler and V. Gold, *Chem. and Ind.*, 1960, 1218.

45 °C,[41] which had k^H/k^D (calculated from k^T/k^D) equal to 6·2 (±0·5),[42] and of 3·74 or 4·0 for the exchange of α-tritiotoluenes with lithium cyclohexylamide in cyclohexylamine at 50 °C.[42,43] However, the reaction constants found for the equilibrium ionisation of 2-substituted fluorenes (6·3—7·5) [23] and three series of derivatives of phenylacetic acid (5·85, 4·82, and 5·15) [44] in aqueous dimethyl sulphoxide are much larger. A ρ value for the theoretical ' ionisation equilibrium ' of the allylbenzenes can be estimated from the latter values to be *ca.* twice that ρ value observed for the rearrangement, it being assumed that the response of the allylic carbanion is similar to that of the other carbon acids above. Two limiting conditions of the transition state for the rearrangement could account for this. First, the carbanion could be approximately half-formed, with the substituents only assisting in delocalisation of *ca.* half the total charge to be finally developed. Secondly, the carbanion could be almost completely formed but the charge being in an orbital having hybridisation between sp^2 and sp^3 on the carbon directly involved in the ionisation reaction.[2] The substituents would then only be able to assist in the formation of the partially delocalised carbanion to a much smaller extent than in the full ' ionisation equilibrium.' The latter explanation appears more likely and, overall, this evidence indicates the proton-abstraction process as the slow rate-determining step.

pK_a *Values of the Carbon Acids*.—It is possible to extrapolate the rate coefficients for the two rearrangements to aqueous solution with $H_- \equiv \text{pH} \equiv 12{\cdot}04$. The ' calculated ' p$K_a$ values of allylbenzene and 1,3,3-triphenylprop-1-yne can be evaluated if a value of k_{-1} can be assumed. Stewart and Jones,[11] assuming that the reverse process for ionisation must be close to the limiting value, estimated k_{-1} to be 10^{10} when calculating the pK_a of dimethyl sulphoxide.* Use of equation (8)

$$K_a = (k_1/k_{-1})(K_w/[H_2O]) \qquad (8)$$

gives ' calculated ' pK_a values of allylbenzene and 1,3,3-triphenylprop-1-yne of *ca.* 34 and 29, respectively.

As it is not possible to measure these values directly, estimates can be made from the values of related carbon acids [23,46] to give the pK_a values of allylbenzene and 1,3,3-triphenylprop-1-yne as 33 (±2) and 26·5 (±2), respectively. These are in good agreement with the ' calculated ' values.

In conclusion, both rearrangements appear to proceed *via* a rate-determining ionisation step. The transition states appear to be highly ' advanced ' and consist of an almost fully formed carbanion.

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* Recent evidence [45] suggests that the reprotonation of a related carbanion in methanol must be well below the diffusion-controlled limit. If this is so for our systems, the pK_a values ' calculated ' are only upper limits as the assumed k_{-1} will be too large.

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