Kinetics and Mechanism of Addition of Acids to Olefins. Part I. Addition of Acetic Acid to Cyclic and Strained Bicyclic Olefins Catalysed by Trifluoromethanesulphonic Acid

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The acid-catalysed addition of acetic acid to some cyclic and strained bicyclic olefins has been investigated using trifluoromethanesulphonic acid as the catalyst. For norbornene and related derivatives, the reaction rate was first order with respect to the catalyst acid but for cyclohexene there was evidence of a small contribution from a second-order term. The addition was essentially non-stereospecific. Values of the kinetic isotope effect were less than unity for cyclic substrates but greater than unity for norbornene suggesting a change to rate-determining proton transfer. Activation parameters are reported together with new values for the acidity function H_0 for CF_3SO_3H in acetic acid. The addition is discussed in terms of intimate and solvent-separated ion-pairs.

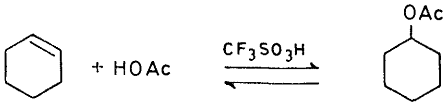
ELECTROPHILIC addition to olefins has been the subject of much interest for many years, though it is only comparatively recently that detailed mechanistic studies of these reactions have been undertaken. The topic has been the subject of two recent comprehensive reviews.[1,2] Acid-catalysed hydration of olefins has received much attention and more recently additions in nonaqueous media such as acetic acid have been investigated, particularly the addition of acetic acid to olefins catalysed by strong acids such as H_2SO_4, HBr, and $HClO_4$. Trifluoromethanesulphonic acid (triflic acid)[3] is the strongest proton acid known in solvent acetic acid[4] which enables the normally slow reaction of cycloalkenes to be followed more conveniently. The purpose of this paper is to examine in detail the addition of acetic acid to cycloalkenes and also to more strained olefins such as norbornene and related compounds using triflic acid as catalyst.

RESULTS

Triflic acid has an acid dissociation constant of 1.26×10^{-5} in solvent acetic acid compared with values of 6.4×10^{-6}, 5.1×10^{-7}, and 10^{-9} for $HClO_4$,[4] CH_3SO_3H,[4] and H_2SO_4.[5] Triflic acid has the advantages that it can be readily purified by distillation and is not a strong oxidant. Also the triflate anion is a very weak nucleophile rendering anion-assisted pathways unlikely (*cf.* halogen acids).

The addition reactions were followed initially by three independent techniques namely ^1H n.m.r. (by loss of olefinic proton signals), g.l.c. (monitoring loss of substrate and appearance of product acetate), and iodimetry. The latter method was found to be more convenient and also more accurate. All three methods led to values of pseudo-first-order rate constants k_ψ within a ±5% range for a given acid concentration. The catalyst acid concentration remained constant during the reaction.

Reaction Products.—It was apparent that for the less-reactive substrates such as cyclopentene and cyclohexene, reaction was incomplete (96 and 93% reaction respectively), and the system comes to equilibrium:

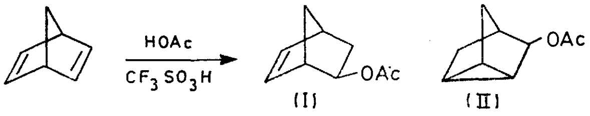


(1)

This was demonstrated by conducting the reverse reaction in the presence of a suitable concentration of catalyst acid. At equilibrium, 7% cyclohexene was formed from cyclohexyl acetate. Also with the less-reactive substrates, reaction solutions darkened appreciably with time. What causes this behaviour is unknown, though it may be associated with the formation of a minor high-boiling product revealed by g.l.c. analysis of the cyclopentene reaction mixture. Mass-spectral analysis indicated the presence of cyclopentyl triflate. The [triflate] : [acetate] product ratio was fairly constant at 0.117 ± 0.004 over the first 20% reaction, but thereafter it decreased until at equilibrium no triflate was observed. It seems probable that the triflate is slowly solvolysed under the reaction conditions in keeping with the findings of von R. Schleyer.[6]

The reactions were also conducted in an inert atmosphere using triply degassed solvent, but no significant differences in rate were observed, ruling out a radical process.

Norbornadiene reacted as follows:



(2)

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[1] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 237.

[2] R. Bolton, 'Comprehensive Chemical Kinetics,' eds. G. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973, vol. 9, p. 1.

[3] A. Streitwieser, jun., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1598.

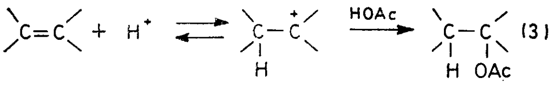
[4] T. Gramstad, *Tidsskr. Kjemi, Bergvsen Met.*, 1959, **30**, 62.

[5] N. F. Hall and R. Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 239.

[6] T. Mun Su, W. F. Sliwinski, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1969, **91**, 5386.

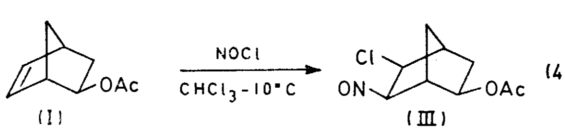
The ratio (I) : (II) was constant at 0.186 ± 0.002 [*i.e.* 15.7% (I)] over the entire course of the reaction. This figure compares with values of 0.31—0.56 (23 °C) and 0.14 (50 °C) for catalysis by H_2SO_4 and $HClO_4$ respectively.[7,*] No di-adduct was found under the reaction conditions used in this work.

One possible mechanism for the addition is the reversible formation of a carbonium ion followed by nucleophilic attack by solvent:

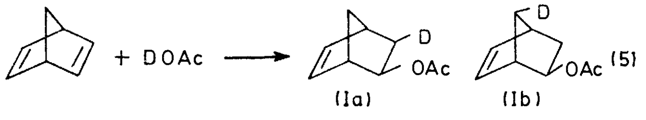


Such a mechanism implies that deuterium should be incorporated into the reactant during reaction in deuteriated media. Accordingly, both cyclopentene and norbornadiene were recovered from 50% conversion reaction mixtures in DOAc and in each case no significant deuterium incorporation (<2%) was observed by ^{1}H n.m.r. and mass spectrometric assays. Thus in any intermediate formed, the incoming proton does not become equivalent to those already present in the molecule. This finding is in accord with the observation of Purlee and Taft[8] in the hydration of 2-methylbut-1-ene, where a π-complex between the olefin and proton was postulated.

Cyclopentene gave a 50% mixture of *cis*- and *trans*-addition products as determined from deuterium magnetic resonance studies on cyclopentanol obtained by $LiAlH_4$ cleavage of cyclopentyl acetate obtained from reaction in acetic [^{2}H]acid. Additionally, by conducting the reaction in *ca.* 50 atomic % deuteriated solvent, it was possible to estimate by a ^{1}H n.m.r. technique the percentage deuteriation of the reaction products. A value of 56 ± 2% ^{2}H incorporation from 46.0 atomic % deuteriated solvent was obtained for the cyclopentene system giving a product isotope ratio κ_H/κ_D † of 0.67 ± 0.05 which is in reasonable agreement with the observed k.s.i.e. for this reaction of 0.75. A more accurate estimate of monodeuteriation was attempted by mass-spectral analysis but matters were complicated by the appearance of an $M + 1$ peak of variable intensity in the spectrum of undeuteriated cyclopentyl acetate. The products of addition to norbornadiene, (I) and (II), were separated by converting (I) into the nitrosyl chloride adduct (III).[9,‡] This reaction has been shown to involve no rearrangement.[9] 1-Chloro-2-nitrosocyclopentane exists as a dimer in the gas phase.[10] Dimer peaks were observed in the mass spectrum of (III) at 50 eV but disappeared at 16 eV. It was possible to evaluate the degree of monodeuteriation and hence the product isotope ratio κ_H/κ_D in solvents of varying deuterium content. Values of 2.2—2.4 were obtained. Mass-spectral analysis also enabled the degree of Wagner–Meerwein rearrangement (Ib) to be evaluated. Approximately 50% of the deuterium label appeared at C-7 indicating a substantial lifetime for the intermediate carbonium-ion or ion-pair.



(I) (III)



(Ia) (Ib)

A similar analysis of nortricyclyl acetate (II) gave a κ_H/κ_D value of 2.3. Compound (II) appears to fragment *via* a cycloheptatriene ion ($C_7H_7^+$) in which complete scrambling of hydrogens occurs.[11]

Reaction Kinetics.—All substrates exhibited good pseudo-first-order plots for upwards of 80% reaction. Corriu[12] in his study of the addition of HOAc to cyclohexene using $HClO_4$, H_2SO_4, and CH_3SO_3H as catalyst acids found some evidence of general acid catalysis from plots of $k_\psi[\mathrm{HA}]^{-\frac{1}{2}}$ *vs.* $[\mathrm{HA}]^{-\frac{1}{2}}$ where k_ψ is the pseudo-first-order rate constant and [HA] is the stoicheiometric concentration of catalyst. However, the actual concentration ranges used were small and some slight curvature in the plots can be discerned. In the present work k_ψ was found to be linearly dependent on [HA] up to 0.3M (see Table 1). Thereafter small positive deviations occur due possibly to the increasing dominance of a third-order term as shown in (6). A

$$v = k_2[\mathrm{S}][\mathrm{HA}] + k_3[\mathrm{S}][\mathrm{HA}]^2 \qquad (6)$$

plot of $k_\psi[\mathrm{HA}]^{-1}$ *vs.* [HA] gave a straight line of slope $k_3 = 0.9 \times 10^{-4}$ l^2 mol^{-2} s^{-1} and intercept $k_2 = 2.9 \times 10^{-4}$ l mol^{-1} s^{-1} (45.4 °C). No such behaviour was observed for norbornene. Triflic acid in acetic acid is probably fully ionised but very incompletely dissociated. If

$$\mathrm{CF_3SO_3H + HOAc \rightleftharpoons (CF_3SO_3^{-}\overset{+}{H})_{HOAc} \rightleftharpoons} \\ \mathrm{\ldots\ldots \rightleftharpoons CF_3SO_3^{-} + \overset{+}{H}_2OAc} \qquad (7)$$

$\overset{+}{\mathrm{H}}_2$OAc were the proton source, then k_ψ would be linearly dependent on $[\mathrm{CF_3SO_3H}]^{\frac{1}{2}}$, which is not observed. On the other hand, if the process were anion assisted the observed linear dependence on $[\mathrm{CF_3SO_3H}]$ could be explained. However, the triflate anion is an extremely weak nucleophile and nucleophilic assistance is likely to be minimal. One other possibility exists, namely attack by molecular or more probably ion paired CF_3SO_3H. Kinetic solvent-isotope effects (k.s.i.e.) were obtained by running reactions in acetic [^{1}H]acid (96.0 atomic % ^{2}H) and the following k_H/k_D values obtained: cyclopentene (0.75 ± 0.03, norbornene 1.58 ± 0.05, and norbornadiene 1.60 ± 0.05).

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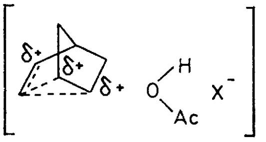
[*] Cristol has proposed that the product-forming steps for (I) and (II) involve the collapse of the solvent-separated ion-pair to give either the conjugate acid of (I) [and hence (I)] or the intimate ion-pair from which (II) is generated presumably by attack from the least-hindered site. Thus the latter process becomes easier as the nucleophilicity of the anion X decreases.



[†] $\kappa_H/\kappa_D = \dfrac{[\mathrm{RH}]}{[\mathrm{RD}]} \cdot \dfrac{[\mathrm{CH_3CO_2D}]}{[\mathrm{CH_3CO_2H}]}$.

[‡] The adduct is probably a mixture of 5-chloro-6-nitroso- and 6-chloro-5-nitroso-norbornen-2-yl acetates.

[7] S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, 1966, **31**, 2726.

[8] E. L. Purlee and R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1956, **78**, 5807.

[9] J. B. Miller, *J. Org. Chem.*, 1961, **26**, 4905.

[10] J. C. Tou and K. Y. Chang, *Org. Mass Spectrometry*, 1970, **3**, 1055.

[11] S. Meyerson, *J. Amer. Chem. Soc.*, 1963, **85**, 3340.

[12] R. Corriu and J. Guenzet, *Tetrahedron*, 1970, **26**, 671.

Triflic Acid–Acetic Acid Complexes.—Distillation of mixtures of the two acids yields a complex of stoicheiometry $CH_3CO_2H\cdot 2CF_3SO_3H$. From preliminary studies of viscosity and ^1H n.m.r. spectra of such solutions, points of inflection occur at *ca.* 50 mol % CF_3SO_3H and cryoscopic measurements indicate polymeric chains of approximately ten units in length, which is in keeping with the very marked increase in viscosity of acid solution greater than 1M. Work is in hand in these laboratories to put these findings on a more quantitative basis.

TABLE 1

Variation of k_ψ (s^{-1}) with [CF_3SO_3H] (M) and H_0 for the addition of acetic acid to cyclohexene and norbornene

	[CF_3SO_3H]	10^4k_ψ	10^4k_ψ/[CF_3SO_3H]	log k_ψ	log [CF_3SO_3H]	H_0
Cyclohexene						
T = 45.4 °C	0.054	0.20	3.70	−4.699	−1.270	−1.94
	0.161	0.49	3.04	−4.310	−0.793	−2.56
	0.268	0.83	3.10	−4.079	−0.572	−2.85
	0.268	0.85	3.17	−4.071	−0.572	−2.85
	0.322	1.03	3.20	−3.987	−0.492	−2.95
	0.376	1.23	3.27	−3.910	−0.425	−3.04
	0.430	1.42	3.30	−3.848	−0.367	−3.12
	0.483	1.62	3.35	−3.790	−0.316	−3.18
T = 25.0 °C	0.227	0.073	0.321	−5.317	−0.644	−2.76
	0.348	0.115	0.330	−4.939	−0.458	−2.99
	0.453	0.153	0.336	−4.815	−0.343	−3.15
Norbornene						
T = 45.4 °C	0.002 31	3.5	1 520	−3.456	−2.636	−0.61 [a]
	0.003 47	5.4	1 550	−3.267	−2.460	−0.76
	0.005 78	8.2	1 420	−3.086	−2.238	−0.95
	0.011 6	16.2	1 400	−2.790	−1.937	−1.21
	0.017 3	25.4	1 470	−2.596	−1.760	−1.36
	0.023 1	34.5	1 490	−2.462	−1.635	−1.47

[a] H_0 from ref. 4.

TABLE 2

Arrhenius parameters $\Delta H^{\ddagger}$ (kcal mol^{-1}) and $\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1}) for the addition of acetic acid to various olefins

Compound	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ (at 25 °C)
Cyclohexene	20.4 ± 0.6	−10.3 ± 1.9
Cyclopentene	19.6 ± 0.2	−12.5 ± 0.6
Norborn-2-ene [b]	18.1 ± 0.5	−5.7 ± 1.8
1,4-Dihydro-1,4-methanonaphthalene	22.8 ± 0.4	+2.3 ± 1.2
Norbornadiene	19.6 ± 0.3	−2.2 ± 1.0
(+) - (R)-Limonene	16.6 ± 1.1	−6.4 ± 3.6
(+) - (R)-Limonene [c]	11.6 ± 0.5	−32.9 ± 1.5
Hept-1-ene [d]	13.4	−32

[a] Errors obtained from least-squares programme. [b] Data corrected statistically for two double-bonds. [c] For addition of CF_3CO_2H in solvent cyclohexane (ref. 21). [d] Ref 13.

DISCUSSION

The bicyclic olefins in general reacted much faster than their monocyclic counterparts as shown by the relative second-order constants (k_{rel}) at 45.4 °C: norbornene (k_{rel} 600) > norbornadiene (276) > benzonorbornadiene (11.5) > cyclopentene (1.0) ~ cyclohexane (1.0). Solvent isotope effects and activation parameters (Table 2) suggest a different mechanism for the bicyclic olefins. In particular, the observed k.s.i.e. for norbornene suggests rate-determining proton transfer whereas the value for cyclopentene (0.75) does not. Acid-catalysed processes can be written in the following general form:

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \qquad (8)$$

$$\text{products} \xleftarrow[\text{A1}]{k_1} SH^+ \xrightarrow[\text{A2}]{\text{solvent } k_2} \text{products} \qquad (9)$$

K.s.i.e. values for $A1$ processes lie typically in the range 0.3—0.5, the value being determined largely by equilibrium (8), since unimolecular decompositions are not generally subject to a pronounced isotope effect.[14] For $A2$ mechanisms, values closer to unity have been found resulting from an isotope effect greater than unity for the reaction of solvent with the conjugate acid SH^+. The value obtained for cyclopentene lies well within this range. A crude calculation of the isotope effect pertaining to equation (8) can be made using the Bunton–Shiner approach.[15] The pK_a of triflic acid is 4.2 which used in conjunction with the autoprotolysis constant (K_A) for acetic acid (pK_A = 12.8)[16] and after statistical correction, gives pK_b of the triflate anion as 9.1. This enables the ν(OH) frequencies of all species, including hydrogen-bonded solvent molecules, to be evaluated and hence a value of the solvent isotope effect for equilibrium (8) to be computed. If it is assumed that a carbonium ion is fully formed as in equation (3) then the isotope effect is *ca.* 0.22 for direct proton transfer from triflic acid. This value increases to *ca.* 1.0 for weak C–H bond formation. The calculated s.i.e. for proton transfer from $CH_3CO_2\overset{+}{H}_2$ lies in a significantly lower range (*cf.* the greater acidity of $D_3{}^+O$ compared

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[13] P. E. Peterson and G. Allen, *J. Amer. Chem. Soc.*, 1963, **85**, 3608.

[14] R. E. Robertson and P. M. Laughton, *Canad. J. Chem.*, 1957, **35**, 1319.

[15] C. A. Bunton and V. J. Shiner, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 42.

[16] B. M. Rode, A. Engelbrecht, and J. Schantl, *Z. phys. Chem. (Leipzig)*, 1973, **253**, 17.

with H_3^+O). One drawback to this treatment is the neglect of entropy terms arising from solvent structure reorganisation[17] which has the effect of increasing the s.i.e. for solvent water. Recently data has become available for the s.i.e. for the dimerisation of acetic acid.[18]

$$2CH_3CO_2H \rightleftharpoons (CH_3CO_2H)_2 \qquad (10)$$

The enthalpy difference $\Delta\Delta H^*$ at 25 °C was -500 cal mol— and the entropy difference ($T\Delta\Delta S$) was $+200$ cal mol—. Thus enthalpy factors dominate but not to the exclusion of entropy contributions. The overall s.i.e. at 25 °C is 0.81.

Pasto *et al.*[19] have used the Bunton–Shiner method to rationalise the low observed k.s.i.e. of 0.48 for the addition of HBr to 1,2-disubstituted olefins in solvent acetic acid, a reaction they classify as Ad_E3 and in which it is suggested that molecular attack involving two molecules of HBr occurs resulting in dominant *anti*-addition. Fahey and his co-workers[20] have reported similar findings. The k.s.i.e. was explained in terms of loss of one ν(HBr) (2 500 cm^{-1}) and gain of one ν(CH) mode (2 900 cm^{-1}). However, the nature of the attacking species is still open to question since, although HBr is only weakly dissociated in acetic acid, it is likely that ion pairs are formed to a significant extent. It is, therefore, arguable as to whether or not a full ν(HBr) is lost. It would appear hazardous to make a distinction between rate-determining proton transfer (A–S_E2) and an $A2$ process since both mechanisms could, depending on detail, accommodate the observed k.s.i.e.

In the case of catalysis by triflic acid (TfOH), a ν(OH) is lost and it is extremely difficult to invoke rate-determining proton transfer for cyclopentene which in terms of the rather simplistic arguments above should lead to a k.s.i.e. of greater than unity. Such k.s.i.e. values have been observed for reactions which almost certainly involve molecular addition *viz.* the addition of CF_3CO_2H to (+)-(R)-limonene in cyclohexane[21] gave a k_H/k_D of 2.5.

A further difference between HBr- and TfOH-catalysed additions is the lack of stereospecificity displayed by the latter. This, in turn, implies the existence of either a free carbonium ion or loose ion-pair in the product-forming step. Any ionic mechanism in a solvent such as acetic acid must take account of ion-pair formation. The overall reaction can be written in general terms as shown below, where species $(\overset{+}{A}\cdot\overset{-}{B})$ and $(\overset{+}{A}||\overset{-}{B})$ refer to intimate and solvent-separated ion-pairs respectively. $(Tf\overset{-}{O}\cdot\overset{+}{H}\cdot S)$ could well be formulated as the π-complex postulated by Taft[8] *e.g.* $[{>}C\overset{\overset{H}{\uparrow}}{=}C{<}]^+\ \bar{O}Tf$ where only the proton bonded *via* the π-orbital undergoes exchange with the solvent, in keeping with the observed lack of incorporation of deuterium in the olefin. Step (12) is unlikely to be rate determining. Step (13) represents the transfer of proton from a π-bonded to a σ-bonded state. If such a process were rate determining then a

$$TfOH \rightleftharpoons (Tf\overset{-}{O}\cdot\overset{+}{H}) \qquad (11)$$

$$(Tf\overset{-}{O}\cdot\overset{+}{H}) + S \underset{}{\overset{k_1}{\rightleftharpoons}} (Tf\overset{-}{O}\cdot\overset{+}{H}\cdot S) \qquad (12)$$

$$(Tf\overset{-}{O}\cdot\overset{+}{H}\cdot S) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (Tf\overset{-}{O}\cdot\overset{+}{H}S) \qquad (13)$$

$$(Tf\overset{-}{O}\cdot\overset{+}{H}S) + HOAc \xrightarrow{k_3} (Tf\overset{-}{O}||\overset{+}{H}S) \qquad (14)$$

$$(Tf\overset{-}{O}||\overset{+}{H}S) \xrightarrow{\text{fast}} (Tf\overset{-}{O}\cdot\overset{+}{H}) + \text{product acetates} \qquad (15)$$

k.s.i.e. of about two would be expected as found for internal hydrogen migrations.[22] On the basis of the observed k.s.i.e. for cyclopentene of 0.75 it seems likely that step (14) is rate determining; that is the conversion of an intimate to a solvent-separated ion-pair. The former could also collapse to give the product triflate which accounts for some 10% of the initial products. Alternatively, the triflate may be formed *via* the process which is second order in catalyst acid analogous to that postulated by Pasto *et al.*[19] Further work is needed to clarify this point. It seems, however, that most intimate ions go on to form a series of solvent-separated ions from which the acetate products are formed with complete lack of stereospecificity. For the bicyclic olefins, step (13) becomes rate determining ($k_H/k_D = 1.6$) due perhaps to the greater stability of the incipient carbon ion-pair. It is interesting that κ_H/κ_D is greater than k_H/k_D for norbornadiene but the ratios are the same for cyclopentene. Any mechanism involving a reversible protonation and hence exchange with solvent would result in a κ_H/κ_D of unity. A–S_E2 reactions usually show $\kappa_H/\kappa_D > k_Hk_D > 1$[23] for reactions in aqueous media. For norbornadiene there is evidence of complete scrambling of deuterium label between C-3 and C-7 in the product acetates which supports the postulate of a relatively long-lived solvent-separated ion-pair as a precursor of the products.†

The $\Delta S^‡$ values obtained for the monocyclic olefins are noticeably more negative than those of the bicyclic series which tends to support a change from an $A2$ to an A–S_E2 mechanism[23-25] though it must be emphasised that most of the reported data refer to solvent water.

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* $\Delta\Delta H = \Delta H_D - \Delta H_H$.

† The stereospecificity of addition has not been established for norbornadiene in this system, though from evidence cited in ref. 7 it would seem likely that *cis-exo*-addition occurs.

[17] P. M. Laughton and R. E. Robertson in 'Solute–Solvent Interations,' eds. J. F. Coetzee and C. D. Ritchie, M. Dekker, New York, 1969, p. 399.

[18] J. Bournay and Y. Marechal, *J. Chem. Phys.*, 1973, **59**, 5077.

[19] D. J. Pasto, G. R. Meyer, and B. Lepeska, *J. Amer. Chem. Soc.*, 1974, **96**, 1858.

[20] R. C. Fahey, C. A. McPherson, and R. A. Smith, *J. Amer. Chem. Soc.*, 1974, **96**, 4534.

[21] R. M. G. Roberts, *J.C.S. Perkin II*, 1976, in the press.

[22] P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.*, 1956, **78**, 1448.

[23] J. M. Williams, jun., and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1968, **6**, 63.

[24] S. Bruckenstein, *J. Amer. Chem. Soc.*, 1960, **82**, 307.

[25] L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.

An examination of the activation parameters for the reaction of (+)-(*R*)-limonene with (*a*) triflic acid–acetic acid and with (*b*) trifluoroacetic acid in cyclohexane (Table 2) it is apparent that the latter reaction is slower by virtue of a highly unfavourable $\Delta S^\ddagger$. There is evidence to suggest that (*b*) proceeds *via* an 'open' dimer of CF_3CO_2H by essentially molecular addition.[21] In acetic acid CF_3CO_2H is some 10^4 times less effective a catalyst than triflic acid, which seems to support the thesis that an ionic form of the catalyst acid is the reaction species.

Finally, plots were made of log k_ψ against both log $[CF_3SO_3H]$ and $-H_0$ (Table 1). For cyclohexene at $[CF_3SO_3H] \leqslant 0.35$M (to avoid possible complications from the third-order term) slopes of 1.09 and 0.79 were obtained. The values of the slopes would seem to favour an $A2$ rather than A–S_E2 mechanism though the evidence is by no means conclusive. The slope of the H_0 plot did not vary significantly when the less extensive data obtained at 25 °C were used. Corresponding slopes for norbornene were 0.99 and 1.08, values which certainly do not allow such distinctions to be made.

EXPERIMENTAL

Purification and Preparation of Starting Materials.—Cyclopentene, cyclohexene, (+)-(*R*)-limonene and norbornadiene were redistilled prior to use and stored under nitrogen at 0 °C. Benzonorbornadiene (1,4-dihydro-1,4-methanonaphthalene) was prepared by a Diels–Alder addition of benzyne, generated *in situ* from anthranilic acid and isopentyl nitrite,[26] to cyclopentadiene. Cyclopentyl and cyclohexyl acetates were prepared by standard procedures.[27] AnalaR grade acetic anhydride and trifluoromethanesulphonic acid were fractionated before use.

Purification of Acetic Acid.—Since reaction rates were sensitive to moisture (Table 3) the solvent was rigorously dried by refluxing over P_2O_5 followed by two fractional distillations. Alternatively, 1% acetic anhydride was added to redistilled AnalaR glacial acetic acid. Both solvent batches gave reproducible results.

TABLE 3

Effect of added acetic anhydride on rates of addition of acetic acid [a] to norborn-2-ene at 25 °C

10^2k_{HA}/l mol^{-1} s^{-1}	0.64	0.21	1.45	1.86	1.98	1.95
$[Ac_2O]$/mol l^{-1}	0.0	0.0 [b]	0.050	0.091	0.156	0.218

[a] Redistilled AnalaR glacial acetic acid. [b] Added 0.118M-H_2O.

Preparation of Acetic [^{2}H]*Acid.*—Acetic anhydride (519.5 g, 5.08 mol) was stirred with *ca.* 0.5 ml of 20% (w/w) DCl–D_2O and deuterium oxide (99.7 atomic % ^{2}H, 101.8 g, 5.08 mol) added dropwise with vigorous stirring. The mixture was warmed gently until reaction commenced after the addition of *ca.* 20 ml of D_2O. When the addition was complete, the mixture was distilled and the distillate fractionated to give 96—98.5 atomic % deuteriated solvent as determined from n.m.r. measurements. 1% Acetic anhydride was added to remove any excess of water.*

Preparation of Triflic [^{2}H]*Acid.*—The anhydride (b.p. 84—85 °C) of the acid was first formed by distilling a mixture of triflic acid and excess of phosphoric oxide. Triflic acid anhydride (18.2 g, 0.064 mol) and deuterium oxide (99.7 atomic % ^{2}H, 1.20 g, 0.060 mol) were mixed and refluxed for 1 h then fractionated to give 77% triflic [^{2}H]acid (b.p. 163—163.5 °C, 99.4 atomic % ^{2}H). It was noted that the deuterium content of a 0.5M-solution of triflic [^{2}H]acid in acetic [^{2}H]acid fell from 96.3 to 79 atomic % ^{2}H over a period of 30 days at room temperature, due to the exchange.† As a result, solutions of triflic acid in the deuteriated solvent were made up immediately prior to use.

$$\mathrm{CH_3CO_2D \rightleftharpoons CH_2DCO_2H} \tag{16}$$

Kinetic Procedure.—Stock solutions of the olefin (1M) and triflic acid (0.5M) were made up in the solvent containing *ca.* 1% acetic anhydride at the desired temperature. Appropriate volumes of each solution were mixed and 1 ml portions withdrawn at suitable times and run into 2 ml of 0.12M-bromine in dry acetic acid containing an excess of lithium bromide. The mixture was shaken for 30 s and then treated with 2 ml of 10% KI and 2 ml of $CHCl_3$. The iodine liberated was titrated against standard sodium thiosulphate using starch as indicator. Control experiments showed that all the olefins used could be assayed quantitatively using this method. Reactions were also monitored using n.m.r. and g.l.c. methods. The reaction was quenched by running portions into water–carbon tetrachloride mixtures. The CCl_4 layer was washed with water, dried, and an n.m.r. spectrum run. The progress of the reaction of cyclopentene and cyclohexene were followed by measuring the decrease in the olefinic signals, using a Varian EM 360 n.m.r. spectrometer. Values of k_{HA} as determined titrimetrically and by n.m.r. agreed to within ±5%. The same CCl_4 solutions for the cyclopentene reaction were analysed by g.l.c. using a Perkin-Elmer F11 instrument and an Apiezon column at 140 °C, calibrations being made with standard solutions of the olefin and the corresponding acetate. The CCl_4 peaks were used as internal standards to calibrate the injections. The rate of consumption of cyclopentene was somewhat different from the rate of formation of cyclopentyl acetate (see Table 4) and another higher-boiling product was observed in the initial stages of the reaction. Mass-spectral analysis indicated that it was probably cyclopentyl triflate. As the reaction proceeded, the triflate gradually disappeared and

TABLE 4

Showing the rate of consumption of cyclopentene and the rate of appearance of products in the reaction with triflic acid (0.278M) in acetic acid at 25 °C

T/h	[Cyclopentene]/M	[Cyclopentyl acetate]/M	[Cyclopentyl triflate]/M [a]
0	0.100	0.000	0.000
1.5	0.091	0.007 5	0.001 5
3.0	0.080	0.013 5	0.006
4.5	0.075	0.020	0.005
6.0	0.069	0.025	0.005
75	0.003	0.097	0.000

[a] Calculated as the difference between the expected and observed yield of cyclopentyl acetate.

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* Commercially available grades of monodeuteriated acid gave reaction rates up to ten times slower than those obtained for dried solvents.

† The exchange was strongly catalysed by P_2O_5.

[26] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

[27] A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, p. 385.

the final solution showed only cyclopentyl acetate (97%) and some unchanged cyclopentene (*ca.* 3%). However when the reaction was repeated with a ten-fold increase in triflic acid concentration, the yield of the high boiler was only increased by *ca.* 25% in the initial stages of the reaction. This of course may well be due to the greatly increased rate of solvolysis of the triflate which is almost certainly an acid-catalysed process.

Analysis of Products.—Titrimetric and n.m.r. analysis indicated that the addition of acetic acid to cyclohexene proceeded to an equilibrium with 6.1 ± 0.8% olefin remaining. This was checked by carrying out the reaction in reverse using cyclohexyl acetate and 6.0 ± 0.5% olefin was detected. Similar analysis of cyclopentene reactions showed that the addition was 97% complete. Both gave dark-brown solutions. Addition of acetic acid to norbornadiene gave two products as shown in reaction (2), with >98% reaction. The ratio (I)/(II) was constant over the whole reaction range at 0.186 ± 0.002.* Separation of (I) and (II) was found to be rather difficult and the following procedure was adopted.[28]

Norbornadiene (1.68 g, 0.018 2 mol) in acetic acid (25 ml) was added to triflic acid (0.338 g, 0.002 25 mol) in acetic acid (25 ml) and the mixture was kept at 25 °C for 20 h. It was then poured into a mixture of light petroleum (b.p. 30—40 °C) (200 ml) and water (200 ml). The organic layer was separated and washed well with water, aqueous Na_2CO_3, and water, and was then dried ($MgSO_4$). After filtration and removal of solvent by rotary evaporation a bluish oil was formed (2.3 g). This was dissolved in AnalaR chloroform (5 ml) and the solution was cooled to −10 °C; NOCl was then passed through it until a brown colour was produced together with a precipitate. Light petroleum (b.p. 30—40 °C) (5 ml) was added to the mixture at −10 °C which was then stirred for a further 30 min; after this it was filtered to give white crystals (0.15 g) of the nitrosyl chloride adduct of (I), m.p. 158 °C. The filtrate was pumped down to give a blue oil consisting mainly of compound (II) which was isolated by preparative g.l.c. using a Varian 204 instrument with an Apiezon column at 110 °C. It was noted that more concentrated reaction mixtures resulted in significant quantities of the diacetate being formed. The above method was used for partially and fully deuteriated acetic acid and the mass spectra of compounds (I) and (II) for each solvent system were analysed. (The m.p. for derivatives in 51.5 and 98.5 atomic % deuteriated acetic acid were 130 and 138 °C.)

Recovery of Starting Materials.—Unchanged cyclopentene and norbornadiene were recovered from reaction mixtures in DOAc at *ca.* 50% conversion by pouring the latter into water, and separating off the upper oily layer which was then dried and distilled. Both n.m.r. and mass spectral analysis showed that deuterium incorporation was less than 2%.

Mass Spectral Analysis of Products.—*Nortricyclyl acetate* (II). The deuterium content was calculated from the *M* and *M* + 1 peaks (*m*/*e* 152 and 153) making due allowance for natural isotopic abundance of ^{13}C. The principal fragmentation pattern is given in Table 5. The appearance of the spectrum below *m*/*e* 92 was in some important respects very similar to that of cycloheptatriene [29,30] (except for the strong $CH_3\overset{+}{C}O$ peak at *m*/*e* 43). In particular identical intensity relationships were observed for *m*/*e* 37—41, 50—53, and 61—65. This strongly suggests that *m*/*e* 91 has the cycloheptatrienyl ion structure $(C_7H_7)^+$ in which all hydrogens are equivalent. This is shown by the label retentions in Table 6. Also the observed 92/93 ratios agreed reasonably well with the calculated values based on complete equivalence of all hydrogens in the parent ion (Table 7). Thus mass-spectral analysis was not helpful in this instance in the detection of Wagner–Meerwein rearrangement products.

TABLE 5

Principal fragmentation patterns (*m*/*e* >65) of nortricyclyl acetate

Reaction	Fragment lost	Mass change (*m*/*e*)	Metastable
$C_7H_9OCOCH_3{}^{\cdot+} \longrightarrow CH_3CO^{\cdot+}$	C_7H_9O	152 ⟶ 43	12.2
$C_7H_9OCOCH_3{}^{\cdot+} \longrightarrow C_7H_8{}^{\cdot+}$	CH_3CO_2H	152 ⟶ 92	55.7
$C_7H_9OCOCH_3{}^{\cdot+} \longrightarrow C_7H_9OH^{\cdot+}$	$CH_2{=}C{=}O$	152 ⟶ 110 110 ⟶ 92	79.6 76.8
$C_7H_9OH^{\cdot+} \longrightarrow C_7H_8{}^{\cdot+}$	H_2O		
$C_7H_9OH^{\cdot+} \longrightarrow C_5H_6{}^{\cdot+}$	C_2H_4O	110 ⟶ 66	39.6
$C_7H_8{}^{\cdot+} \longrightarrow C_7H_7{}^{+}$	$H^{\cdot}$	92 ⟶ 91	(90.0) [a]
$C_7H_8{}^{\cdot+} \longrightarrow C_5H_6{}^{\cdot+}$	C_2H_2	92 ⟶ 66	(47.3) [a]

[a] Metastable not observed.

TABLE 6

Percentage retention (*R*) of label for fragment ions in the mass spectrum of nortricyclyl acetate (II), the nitrosyl chloride of norborn-2-en-5-yl acetate (III), and cycloheptatriene

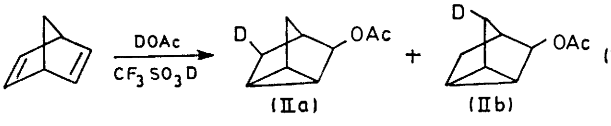
Ion	$C_7H_7{}^+$	$C_6H_5{}^+$	$C_3H_3{}^+$
m/*e*	91	77	39
R(II)	84.0	57.3	31.4
R(III)	61.0	61.5	8.2
R(cycloheptatriene)	89.1	45	39.8
R(statistical)	87.5	62.5	37.5

TABLE 7

Observed and calculated mass peak ratios 92/93 for nortricyclyl acetate (II) and 157/158 for the nitrosyl chloride of norborn-2-en-5-yl acetate (III) from spectra run at 16 eV

For (II)				
%^2H in parent ions	17.4	18.2	78.8	9.34
(92/93) obs.	5.24	4.57	0.49	0.29
(92/93) calc.[a]	5.45	4.62	0.43	0.20
For (III)				
%^2H in parent ions	24.7	37.9	81.3	90.2
(157/158) obs.	4.90	3.91	0.53	0.43
(157/158) calc.[a]	3.55	1.97	0.38	0.25
(157/158) calc.[b]	5.37	2.51	0.63	0.47

[a] Based on 8 equivalent H atoms in the parent ion. [b] Based on 4 equivalent H atoms in the parent ion.



(17)

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* Rearrangement (I) ⟶ (II) did not occur under the experimental conditions.

[28] J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Synth.*, Coll. Vol. V, 1973, 863.

[29] S. Meyerson, *J. Amer. Chem. Soc.*, 1963, **85**, 3340.

[30] S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Amer. Chem. Soc.*, 1960, **83**, 1401.

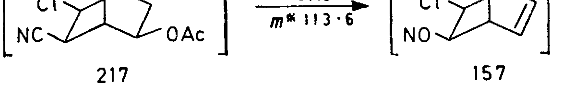
Nitrosyl Chloride of Norborn-2-en-5-yl Acetate (III).—The principal fragmentation pattern is given in Table 8. The following fragments showed typical chlorine isotope patterns: *m/e* 217, 175, 157, 147, and 131. An extremely weak parent ion was observed for the dimer at 454, and at 16 eV the spectrum appeared to be of the monomer only. The partial spectrum in the regions *m/e* 37—41, 50—53, and 61—65 was similar to that of nortricyclyl acetate and cycloheptatriene but the intensity relationships were somewhat different. Table 6 shows that the fragmentation pattern is not that of cycloheptatriene and Table 7 indicates that probably only *four* of the hydrogens (at C-3 and C-7) are equivalent in terms of the reaction [19] which would suggest that the C_7H_8ClON ion retains some of the original bicyclic structure. Weak metastable peaks observed for the 153—66, 153—67 fragmentations are of approximately equal intensity, which suggests almost complete scrambling of deuterium label during the addition reaction which in turn indicates a fairly long lived norbornenyl cation intermediate capable of undergoing rapid Wagner–Meerwein rearrangement.

TABLE 8

Principal fragmentation patterns (*m/e* >65) of the nitrosyl chloride of norborn-2-en-5-yl acetate

Reaction	Fragment lost	(*m/e*)	Metastable
$C_9H_{12}ClO_3N^{\cdot+} \longrightarrow CH_3CO^{\cdot+}$	$C_7H_9ClO_2N$	217 → 43	(8.5) [a]
$C_9H_{12}ClO_3N^{\cdot+} \longrightarrow C_9H_{12}O_2^{\cdot+}$	NOCl	217 → 152	(106.4) [a]
$C_9H_{12}ClO_3N^{\cdot+} \longrightarrow C_7H_8ClON^{\cdot+}$	CH_3CO_2H	217 → 157	113.6
$C_9H_{12}ClO_3N^{\cdot+} \longrightarrow C_7H_{10}ClO_2N^{\cdot+}$	$CH_2{=}C{=}O$	217 → 175	141.1
$C_7H_{10}ClO_2N^{\cdot+} \longrightarrow C_7H_8ClON^{\cdot+}$	H_2O	175 → 157	(140.9) [a]
$C_7H_{10}ClO_2N^{\cdot+} \longrightarrow C_6H_{10}ClON^{\cdot+}$	CO [b]	175 → 147	123.5
$C_7H_{10}ClO_2N^{\cdot+} \longrightarrow C_5H_6ClO_2N^{\cdot+}$	C_2H_4 [b]	175 → 147	123.5
$C_7H_{10}ClO_2N^{\cdot+} \longrightarrow C_5H_6ClON^{\cdot+}$	C_2H_4O	175 → 131	(98.0) [a]
$C_7H_8ClON^{\cdot+} \longrightarrow C_7H_8^{\cdot+}$	NOCl	157 → 92	53.9
$C_9H_{12}O_2^{\cdot+} \longrightarrow C_5H_6^{\cdot+}$	$CH_2{=}CHOAc$	152 → 66	28.6
$C_9H_{12}O_2^{\cdot+} \longrightarrow C_7H_8^{\cdot+}$	CH_3CO_2H	152 → 92	55.7
$C_6H_{10}ClON^{\cdot+} \longrightarrow C_6H_{10}ON^+$	Cl· [b]	147 → 112	85.4
$C_5H_6ClO_2N^{\cdot+} \longrightarrow C_5H_6O_2N$	Cl· [b]	147 → 112	85.4
$C_5H_6ClON^{\cdot+} \longrightarrow C_5H_5ON$	HCl	131 → 95	(68.8) [a]
$C_6H_{10}ON^+ \longrightarrow C_6H_9^+$	HONO [b]	112 → 81	58.6
$C_5H_6O_2N^+ \longrightarrow C_5H_5O^+$	HONO [b]	112 → 81	58.6
$C_7H_8^{\cdot+} \longrightarrow C_7H_7^+$	H·	92 → 91	(90.0) [a]

[a] Metastable not observed. [b] Either CO or C_2H_4 may be eliminated giving rise to two possible fragmentation routes.

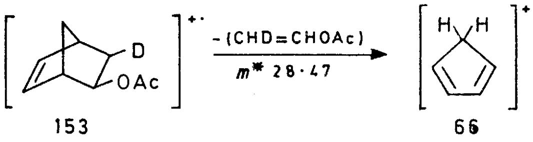


(18)

Acidity Functions.—Values of H_0 were obtained for triflic acid in acetic acid in the range 0.08—0.74M at 25 °C using 2-chloro-6-nitroaniline as indicator (pK_a — 2.43).[31] The indicator was prepared by nitrating 2-chloroacetanilide followed by hydrolysis to give a mixture of the 4- and 6-nitroanilines. The 6-isomer was separated by repeated fractional sublimation to give yellow needles, m.p. 73 °C ($\lambda_{max.}$ 390 nm, $\varepsilon_{max.}$ 4 790 in dry acetic acid). The peak at 390 nm disappeared completely in 1M-CF_3SO_3H. Absorbances were measured at 390 and 420 nm for various triflic acid concentrations in both 'dry' and 'wet' solvent, using solutions of the appropriate acid strength as references. Values of H_0 (Table 9) were obtained using the relationship

$$H_0 = -\log I + pK_a \qquad (22)$$

where $I = [HI^+/(I)]$ is the ionisation ratio of indicator I



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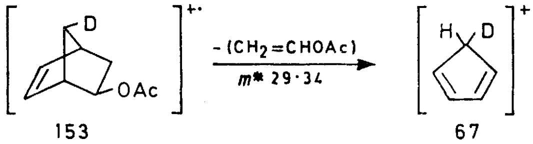

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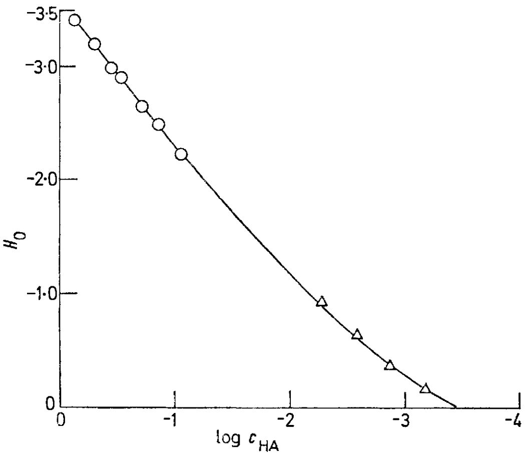
TABLE 9

H_0 Values for triflic acid in glacial acetic acid [a] at 25.1 °C

$[CF_3SO_3H]$/ mol l^{-1}	A_{390} [b]	A_{420}	I_{390} [c]	I_{420}	log I_{av}	H_0
0.0	0.762	0.335				
0.087	0.453	0.219	0.710	0.56	−0.200	−2.23
0.137	0.368	0.161	0.12	0.16	0.057	−2.49
0.189	0.300	0.131	1.63	1.70	0.222	−2.65
0.292	0.203	0.092	3.01	3.00	0.477	−2.91
0.354	0.172	0.083	3.81	3.50	0.562	−2.99
0.498	0.125	0.060	5.89	5.61	0.760	−3.19
0.737	0.091	0.039	9.07	10.5	0.99	−3.42
3.24	0.017	0.011				

[a] Redistilled with 1% Ac_2O added. [b] A is the absorbance of solutions at a given wavelength. [c] I is the indicator ratio.



Showing the compatibility of H_0 values obtained in this paper with those of Gramstad (ref. 4). ○ = data in present work and △ = data from ref. 4.

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[31] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

and K_a is the acid dissociation constant of HI^+. The values of H_0 thus obtained were plotted against log $c_{CF_3SO_3H}$ together with the earlier data of Gramstad[4] obtained at lower concentrations. The two sets of data form a smooth curve (see Figure). Over the range 0.08—0.74M, the plot was linear with slopes of -1.64 and -1.30 for the ' wet ' and ' dry ' solvents respectively.

Acetic Acid–Triflic Acid Complex.—CF_3SO_3H (10.2 g, 0.068 mol) was placed in a small distillation flask and dry glacial acetic acid (4.1 g, 0.068 mol) was added dropwise with exclusion of atmospheric moisture. A strongly exothermic reaction occurred. The mixture was distilled at atmospheric pressure to give a yellow viscous oil (8.0 g) (b.p. 209—210 °C), whose n.m.r. spectrum showed two peaks: CH_3CO ($\delta = 2.47$), OH (13 64) Integration indicated a complex of stoicheiometry $CH_3CO_2H\cdot 2CF_3SO_3H$ (Found: C, 14.5; H, 2.0; F, 31.0; S, 18.1. Calc. for 2 : 1 complex: C, 13.3; H, 1.67; F, 31.7; S, 17.8).

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