

## Kinetics and Mechanism of Addition of Acids to Olefins. Part 2.\* Addition of Trifluoroacetic Acid to (+)-(R)-Limonene in Weakly Polar Media

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A detailed kinetic study has been made of the addition of trifluoroacetic acid to (+)-(R)-limonene in weakly polar solvents. Activation parameters and kinetic isotope effects are reported and the mechanism of the reaction is discussed together with an assessment of the relative importance of the monomeric and dimeric acid species in the reaction.

ALTHOUGH many investigations into the mechanism of addition of acids to olefins have been carried out, surprisingly few have dealt with the kinetics of these processes. Hydration of olefins has received some attention, notably by Taft and his co-workers.<sup>1</sup> More recently the additions of HCl and HBr in solvents, acetic acid,<sup>2</sup> and nitromethane<sup>3</sup> have been studied. Even less data are available for additions in non-polar solvents. Early work on the addition of HCl and HBr to olefins in solvent hexane<sup>4</sup> were hampered by undefined but possibly radical catalytic processes. Where these could be suppressed, an order of three in acid was observed. Since most of the work so far reported has been in polar solvents it was decided to investigate reactions in non-polar media. (+)-(R)-Limonene was chosen as the olefin since the rates of addition are conveniently measurable as opposed to the rather sluggish reactivity of the more generally studied cyclic olefins. Also the reactions could be followed polarimetrically, enabling contributions from ionic (carbonium ion) mechanisms to be evaluated. In view of the complications reported for HBr and HCl additions, trifluoroacetic acid was used as the acidic reagent.

### RESULTS AND DISCUSSION

Trifluoroacetic acid was found to add readily to the  $\Delta^8$  double bond of (+)-(R)-limonene in weakly polar solvents  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , benzene, and cyclohexane, the addition being complete in *ca.* 30 min at 20 °C (1.6M each reagent). Comparable reactions in solvents dioxan, acetone, and  $\text{Me}_2\text{SO}$  gave no appreciable reaction after 24 h under similar conditions.

N.m.r. analysis of reaction products in solvent cyclohexane indicated that the addition was in the Markownikoff sense, shown by the appearance of a new singlet (6 H) at  $\delta$  1.50, and the disappearance of the  $=\text{CH}_2$  signal at  $\delta$  4.65. It was also noted that, on standing, new signals appeared upfield from the *gem*-dimethyl resonance, and that the  $=\text{CH}$  signal at C-2 ( $\delta$  5.34) gradually reduced in intensity. Finally, after 14 days at 40 °C 18% *p*-cymene was detected (sharp aromatic singlet at  $\delta$  7.00). It is clear from these results that extensive rearrangement occurs in the later stages of reaction. Mass-spectral analysis of reactions with  $\text{CF}_3\text{CO}_2\text{H}$  gave high mass peaks at *m/e* 386, 272 corresponding to the

fragmentation of dimeric products by loss of one and two molecules of  $\text{CF}_3\text{CO}_2\text{H}$ .

The reaction was also followed polarimetrically (0.6M each reagent, 40 °C). Values of  $\alpha$  fell rapidly for the first 30 min of reaction, after which, a further though much less rapid fall-off occurred giving after 14 days a value close to zero. By plotting  $\log \alpha_0/\alpha_t$  against time two straight lines could be drawn intersecting at  $t = 17$  min and giving a value of  $\alpha_D$  of 55.8° for (II) [equation (6)]. This correlates well with a value of 54° obtained from a preparation of (II) by mixing (+)-(R)-limonene with  $\text{CF}_3\text{CO}_2\text{H}$ . Using this value, the rate of reaction could be evaluated. The process of racemisation may involve either a hydride shift, or addition of a further molecule of acid to the remaining double bond. The latter would involve complete consumption of  $\text{CF}_3\text{CO}_2\text{H}$  whereas in fact only 72% of the acid is consumed [but *vide infra* equation (6)]. Also the mass spectrum of the products shows no peaks which could be attributed to the di-adduct. *p*-Cymene is probably formed by an acid-catalysed disproportionation reaction.<sup>5</sup>

**Reaction Kinetics.**—The reaction rates in cyclohexane were followed using three independent techniques, (a) <sup>1</sup>H n.m.r., by measuring loss of  $=\text{CH}_2$  signals, (b) polarimetry, using the above value of  $[\alpha]_D$  for the trifluoroacetate product (II), and (c) by direct titration of the acid with standard alkali. In all cases third-order kinetics were observed in accordance with equation (1). The values of  $k_3$  determined by the above methods

$$v = k_3[\text{olefin}][\text{CF}_3\text{CO}_2\text{H}]^2 \quad (1)$$

agreed fairly well within  $\pm 7\%$ . The titrimetric method was the most convenient and most accurate and was subsequently used as the main analytical method. The results are compiled in Table I. The reaction rates were insensitive to the presence of small concentrations of water. Data fitted third-order plots quite precisely over the first 40–50% of the reaction, thereafter the slopes decreased, probably due to the incursion of an acid-liberating process (*vide infra*).

The second-order term in acid could be explained by two possible mechanisms both involving molecular attack. Trifluoroacetic acid exists at least in part as a

\* Part 1, ref. 23.

<sup>1</sup> R. H. Boyd, R. W. Taft, jun., A. D. Wold, and D. R. Christman, *J. Amer. Chem. Soc.*, 1960, **82**, 4729, and preceding papers.

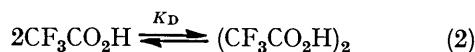
<sup>2</sup> R. C. Fahey, C. A. McPherson, and R. A. Smith, *J. Amer. Chem. Soc.*, 1974, **96**, 4534.

<sup>3</sup> Y. Pocker, K. D. Stevens, and J. J. Champoux, *J. Amer. Chem. Soc.*, 1969, **91**, 4199.

<sup>4</sup> F. R. Mayo and J. J. Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339, 1348.

<sup>5</sup> N. H. Andersen, D. D. Syrdal, and C. Graham, *Tetrahedron Letters*, 1972, **10**, 903.

dimer in non-polar solvents,  $^6 K_D^{25}$  having values of 192, 149, 2.6, and 1.5 l mol<sup>-1</sup> in solvents cyclohexane, CCl<sub>4</sub>,



benzene, and 1,2-dichloroethane, respectively. Addition of the dimer to the olefinic double bond could then occur

TABLE 1

Observed third-order rate constants,  $k_3$  (l<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>) for the reaction of (+)-(R)-limonene with trifluoroacetic acid in cyclohexane

[(+)-(R)-limonene]/M	[CF <sub>3</sub> CO <sub>2</sub> H]/M	θ <sub>c</sub> /°C	10 <sup>2</sup> k <sub>3</sub>	k <sub>H</sub> /k <sub>D</sub>
0.302	0.302	25.0	0.37	
0.302	0.302	25.0	0.147 <sup>a</sup>	2.51
0.297	0.297	31.9	0.59	
0.215	0.297	31.9	0.64	
0.143	0.297	31.9	0.60	
0.604	0.297	31.9	0.59	
0.302	0.302	31.9	0.62 <sup>b</sup>	
0.302	0.302	36.0	0.75	
0.302	0.302	40.0	0.89	
0.302	0.302	44.7	1.32	
0.302	0.302	48.9	1.60	
0.134	0.284	48.9	1.65	
0.302	0.302	48.9	0.712 <sup>a</sup>	2.32

<sup>a</sup> Using 99.7 atomic %D CF<sub>3</sub>CO<sub>2</sub>D. <sup>b</sup> Using cyclohexane saturated with water (~4 × 10<sup>-3</sup>M-H<sub>2</sub>O).

in a rate-limiting step (3). Alternatively an *Ad<sub>E</sub>3* mechanism could be involved,<sup>7</sup> which requires two

it is the monomer and not the dimer which is the reactive species. Christian and Stevens<sup>6</sup> have suggested that

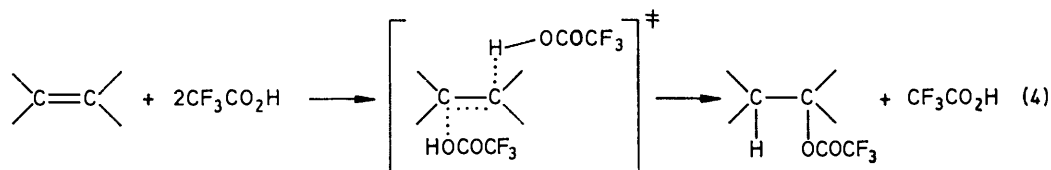
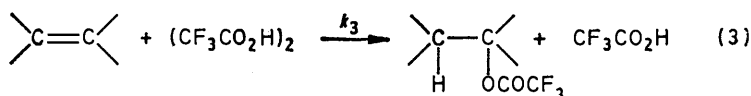
TABLE 2

Observed third-order rate constants,  $k_3$  (l<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>) for the reaction of (+)-(R)-limonene with trifluoroacetic acid in benzene

[(+)-(R)-limonene]/M	[CF <sub>3</sub> CO <sub>2</sub> H]/M	θ <sub>c</sub> /°C	10 <sup>2</sup> k <sub>3</sub>	k <sub>H</sub> /k <sub>D</sub>	(k <sub>H</sub> /k <sub>D</sub> ) <sub>corr</sub> <sup>a</sup>
0.289	0.289	24.2	0.87		
0.284	0.425	24.2	0.87		
0.421	0.281	24.2	0.86		
0.289	0.289 <sup>a</sup>	24.2	0.307		
0.421	0.281 <sup>a</sup>	24.2	0.305		
0.284	0.450 <sup>a</sup>	24.2	0.311	2.81	3.1
0.285	0.285	30.0	1.12		
0.285	0.285 <sup>a</sup>	30.0	0.401	2.81	3.1
0.285	0.285	30.0	0.82 <sup>b</sup>		
0.284	0.284 <sup>a</sup>	34.5	0.528		
0.282	0.282	40.4	1.77		
0.282	0.282 <sup>a</sup>	40.4	0.643	2.75	3.0
0.281	0.281	45.0	2.08		
0.281	0.281 <sup>a</sup>	45.0	0.852	2.45	2.6
0.280	0.280	50.0	2.36		
0.280	0.280 <sup>a</sup>	50.0	1.06	2.20	2.35

<sup>a</sup> Using 95.5 atomic %D CF<sub>3</sub>CO<sub>2</sub>D. <sup>b</sup> Using benzene saturated with water. <sup>c</sup> Corrected to 100.0 at %D CF<sub>3</sub>CO<sub>2</sub>D by assuming linear relationship between  $k_{obs}$  and mole fraction CF<sub>3</sub>CO<sub>2</sub>D.

the dimer is predominantly cyclic. This would seem to support the above thesis, since the acid protons would be strongly hydrogen bonded in such a structure and



molecules of monomeric CF<sub>3</sub>CO<sub>2</sub>H in the transition state as depicted below. Such reactions seem to involve dominantly anti-addition, and are formally the reverse of *E2* reactions. If the dimer were the attacking species, then a change of solvent from cyclohexane to benzene should result in a diminution of rate roughly in accordance with the decrease in  $K_D$ , since the dielectric constants do not vary appreciably ( $\epsilon^{25}$  cyclohexane 2.015; benzene 2.274).<sup>8</sup> However, it was found that

	Cyclohexane	Benzene	1,2-Dichloroethane
$k_3^{\text{rel}}$ (25 °C)	1.00	2.45	7.4

the rates were faster in both benzene and dichloroethane. The data for solvent benzene are listed in Table 2, and a summary of activation and thermodynamic parameters both for the addition and dimerisation appear in Tables 3 and 4. The above rate sequence suggests that

<sup>6</sup> S. D. Christian and T. L. Stevens, *J. Phys. Chem.*, 1972, **76**, 2039.

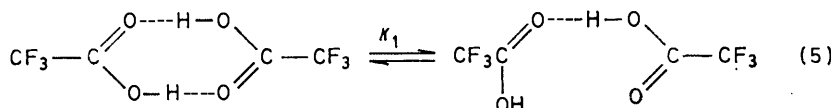
<sup>7</sup> D. J. Pasto, G. R. Meyer, and B. Lapeski, *J. Amer. Chem. Soc.*, 1974, **96**, 1858.

hence less available for reaction. In this context, the lack of reactivity in solvents known to form strong hydrogen-bonded complexes with trifluoroacetic acid, *viz.* Me<sub>2</sub>SO, acetone and dioxan, is significant. One cannot at this stage, however, completely rule out a change of mechanism on going from cyclohexane to benzene. The activation parameters are certainly more different than anticipated, the change being accompanied by a decrease in enthalpy of activation of 3.8 kcal mol<sup>-1</sup> and an increase in negative entropy of activation of 10.9 e.u. Such changes could be rationalised on this basis of change from predominantly dimer to predominantly monomer attack reflecting the increasing dominance of the monomer as the polarity of the medium is increased (9% for cyclohexane, 46.5% for benzene at 0.3M). The increased  $\Delta H^\ddagger$  for cyclohexane could be accounted for by the energy needed to

<sup>8</sup> Handbook of Chemistry and Physics, 54th edn., CRC Press, 1973, p. E54.

open the cyclic dimer, and the more favourable  $\Delta S^\ddagger$  would be a consequence of such a process.

The observed kinetic isotope effects (k.i.e.) lay in the range 2.2—3.1 for all systems studied, and indicate that a proton is transferred in the rate-limiting step. The values of  $k_H/k_D$  for solvent cyclohexane are significantly less than those for solvent benzene. If a dimeric species is the reagent in the former solvent, it will probably be in the 'open' form governed by equilibrium (5).



The k.i.e. for open-dimer attack will be less than that for monomer attack, since the former will still have one fairly strong hydrogen bond present, and could account

TABLE 3

Activation parameters,  $E_a$  (kcal mol<sup>-1</sup>) and  $\Delta S^\ddagger$  (cal K<sup>-1</sup> mol<sup>-1</sup>) for the addition of  $\text{CF}_3\text{CO}_2\text{H}$  to (+)-(R)-limonene and *p*-menth-8-ene in solvents cyclohexane and benzene

Compound	Solvent	$E_a^a$	$\Delta S^\ddagger^b$
(+)-(R)-Limonene	Cyclohexane	11.6 ± 0.5	-32.9 ± 1.5
(+)-(R)-Limonene	Benzene	7.8 ± 0.4	-43.8 ± 2.0
(+)-(R)-Limonene	Benzene	9.2 <sup>c</sup>	-41.4 <sup>c</sup>
		(9.6) <sup>d</sup>	(-40.0) <sup>d</sup>
<i>p</i> -Menth-8-ene	Cyclohexane	11.5 ± 0.5	-33.5 ± 1.7
Oct-1-ene	CF <sub>3</sub> CO <sub>2</sub> H	13.8	-30.0 <sup>e</sup>

<sup>a</sup> Using values of  $k_3$ . <sup>b</sup> Calc. for 25 °C. <sup>c</sup> Addition of CF<sub>3</sub>-CO<sub>2</sub>D. <sup>d</sup> Figures in parentheses refer to  $k_3$  values corrected to 100 atomic %D CF<sub>3</sub>CO<sub>2</sub>D. <sup>e</sup> Ref. 21.

TABLE 4

Enthalpy,  $\Delta H_0$  (kcal mol<sup>-1</sup>), and entropy,  $\Delta S_0$  (cal K<sup>-1</sup> mol<sup>-1</sup>), changes for the dimerisation of  $\text{CF}_3\text{CO}_2\text{H}$  in various solvents<sup>a</sup> together with % monomer at 0.3M at 25°

Solvent	$\Delta H_0$	$\Delta S_0^b$	% Monomer
Cyclohexane	-11.7	-28.9	9.0
CCl <sub>4</sub>	-9.2	-20.8	10.0
Benzene	-7.4 <sup>c</sup>	-22.8	46.5
1,2-Dichloroethane	-7.0	-22.8	63.8

<sup>a</sup> Data from ref. 6. <sup>b</sup> Calc. for 25 °C. <sup>c</sup> Values assumed to be the same as for solvent diphenylmethane.

for the lower  $k_H/k_D$  values in solvent cyclohexane. No values have been reported for such equilibria, though Taylor and Templeman<sup>9</sup> have quoted a figure of 1.1 for dimerisation of trifluoroacetic acid in the vapour phase. During this present work, an attempt was made to determine the isotope effect for dimerisation in cyclohexane, and although the data was not very accurate, due to difficulty in satisfactorily separating the  $\nu(\text{C}=\text{O})$  modes for monomer and dimer, a value of  $1.3 \pm 0.3$  was obtained. The k.i.e. values for cyclohexane and benzene differ by approximately this factor, and lend some

†  $\delta_T \Delta H^\ddagger = \Delta H^\ddagger$  (deuterium) -  $\Delta H^\ddagger$  (protium).

<sup>9</sup> M. D. Taylor and M. B. Templeman, *J. Amer. Chem. Soc.*, 1956, **78**, 2952.

<sup>10</sup> L. W. Reeves, *Canad. J. Chem.*, 1961, **39**, 1711.

<sup>11</sup> T. S. S. R. Murty and K. S. Pitzer, *J. Phys. Chem.*, 1969, **73**, 1426.

support for a change in mechanism, though it must be stressed that specific donor-acceptor complexes formed between the acid and the more basic solvent, benzene, have been neglected in this simple treatment. Such interactions would lower the k.i.e. and thus the real differences between the two solvents may be even greater than those observed experimentally.

It may be possible to distinguish between the two mechanisms by determining the stereochemistry of the

addition since attack by an 'open' dimer would presumably result in *cis*-addition whereas there is already much evidence to suggest that concerted attack by two monomer units is dominantly anti.<sup>7</sup> Work is currently being undertaken to resolve this question. From Table 3,  $\delta_T \Delta H^\ddagger$  and  $\delta_T \Delta S^\ddagger$  have values of +1 800 and +1 130 cal respectively indicating a substantial contribution for the entropy terms.†

The structure of the dimeric species in non-polar solvents has been the subject of much controversy in recent years. In a study of chemical shifts of the acidic protons of a series of carboxylic acids, Reeves<sup>10</sup> interpreted the results in terms of chain-like or open hydrogen-bonded polymers. Murty and Pitzer<sup>11,12</sup> have made a detailed investigation of the  $\nu(\text{OH})$  and  $\nu(\text{C}=\text{O})$  bands of  $\text{CF}_3\text{CO}_2\text{H}$  in solvents benzene and  $\text{CCl}_4$ , and conclude that for the latter solvent an equilibrium exists between open-chain dimers and linear polymeric species, whereas for solvent benzene appreciable amounts of monomer are present below  $10^{-2}\text{M}$ -acid concentrations. The interpretation of the data in benzene has been criticised by Kirszenbaum *et al.*<sup>13</sup> who obtained evidence for cyclic dimers for  $<10^{-2}\text{M}$ -solutions. Evidence supporting monomeric species in benzene comes from the quantitative study of Christian and Stevens<sup>6</sup> who found a value of 2.6 for  $K_D$ . They, however, are again of the opinion that the dimers are mainly cyclic in structure. Unfortunately, there are also wide discrepancies between these values of  $K_D$  obtained from i.r. data and those derived from measurements of dielectric constants<sup>14</sup> (192 and 320 l mol<sup>-1</sup> respectively for solvent cyclohexane at 25 °C). For chlorinated acetic acids, the dielectric constant decreases with increasing acid strength at the same time the amount of dimer present also decreases<sup>4</sup> which suggests that dimer has appreciable polarity, *i.e.* it is open rather than cyclic. The dielectric constant of trifluoroacetic acid is high<sup>15</sup> (43.4 at 27.7 °C) and varies markedly with temperature, which is quite unlike the behaviour of acetic acid which is thought to have a

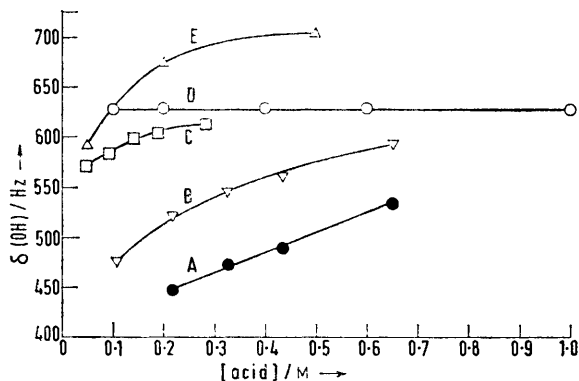
<sup>12</sup> T. S. S. R. Murty, *J. Phys. Chem.*, 1971, **75**, 1330.

<sup>13</sup> M. Kirszenbaum, J. Corset, and M. L. Josien, *J. Phys. Chem.*, 1971, **75**, 1327.

<sup>14</sup> F. Thyron and D. Decroocq, *Compt. rend.*, 1965, 260(7), 2797.

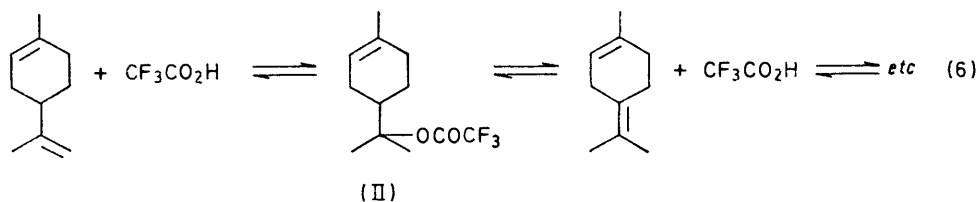
<sup>15</sup> J. H. Simons and K. E. Lorentzen, *J. Amer. Chem. Soc.*, 1950, **72**, 1426.

polymeric structure in non-polar solvents.<sup>16</sup> In this context it is interesting to compare the chemical shifts [ $\delta(\text{OH})$ ] of acidic protons as a function of acid concentrations in the various solvents used in the present study (see Figure). In solvent  $\text{CCl}_4$  where dimers predominate,  $\delta(\text{OH})$  has a maximum value of 710 Hz for



Chemical shifts of hydroxylic protons [ $\delta(\text{OH})$ ] in Hz from  $\text{SiMe}_4$  at 60 MHz in various solvents: curve A —  $\text{CF}_3\text{CO}_2\text{H}$  in benzene, curve B —  $\text{CF}_3\text{CO}_2\text{H}$  in 1,2-dichloroethane, curve C —  $\text{CF}_3\text{SO}_3\text{H}$  in  $\text{CCl}_4$ , curve D —  $\text{CF}_3\text{CO}_2\text{H}$  in nitromethane, and curve E —  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CCl}_4$

$\text{CF}_3\text{CO}_2\text{H}$ . This is considerably less than the chemical shift of strongly hydrogen-bonded complexes such as  $\text{CF}_3\text{CO}_2\text{H}\cdot\text{N}$ -methylformamide (820 Hz)<sup>10</sup> and  $2\text{CF}_3\text{SO}_3\text{H}\cdot\text{CH}_3\text{CO}_2\text{H}$  (818 Hz)<sup>17</sup> and suggests an open



rather than cyclic form.  $\delta(\text{OH})$  Values for monomeric species should be lower than those of the dimers due to the increased shielding by the neighbouring oxygen atom. This effect is shown in the Figure by comparing the shifts in  $\text{CCl}_4$  and 1,2-dichloroethane, the latter having a low  $K_D$  value.  $\delta(\text{OH})$  For  $\text{CF}_3\text{CO}_2\text{H}$  in nitromethane is almost insensitive to concentration changes and has a reasonably high value in keeping with marked hydrogen bonding between acid and solvent. Trifluoromethanesulphonic acid is a much stronger acid than trifluoroacetic acid, yet the latter has higher  $\delta(\text{OH})$  values and indicates that dimer formation is absent in the former. This is in accord with the general observation that dimers are formed most readily by the weaker acids.<sup>14</sup> Thus one cannot rule out the existence of open dimers, since they must be intermediates formed in any equilibrium between monomers and cyclic dimers. Also it must be stressed that most of the work

referred to here relates to dilute solution ( $<10^{-2}\text{M}$ ), whereas the kinetic studies employed acid concentrations of approximately 0.3M.

The reactions in cyclohexane and benzene were strongly catalysed by stannic chloride, and led to the formation of polymeric products, together with the release of acid such that 72.5 and 85.0%  $\text{CF}_3\text{CO}_2\text{H}$  respectively remained after prolonged period of time. Stannic chloride forms 1:2 complexes with carboxylic acids in weakly polar media. I.r. studies indicate that the adducts involve six-co-ordinated tin with a 'half-opened' carboxylic acid dimer acting as a *cis*-chelate.<sup>18</sup> However, the stability of these complexes decreases markedly when electron-withdrawing substituents are present in the acid, and hence in the case of  $\text{CF}_3\text{CO}_2\text{H}$  the complexes must be extremely reactive to produce the observed rate enhancements if indeed they are the major cause of catalysis. An alternative mode of catalysis is the formation of a complex between the olefin and  $\text{SnCl}_4$ .<sup>19</sup> Further work is needed to clarify the mechanism of the catalytic process. In general Brønsted acids are strengthened by the presence of stannic chloride.<sup>20</sup> The enhanced rates with  $\text{SnCl}_4$  coupled with the observation that the addition of  $\text{CF}_3\text{CO}_2\text{H}$  is some 20 times faster than that of  $\text{CCl}_3\text{CO}_2\text{H}$  indicates that proton transfer is mechanistically very important, a thesis supported by the kinetic isotope effects.

Peterson<sup>21</sup> has demonstrated that remote substituents

(particularly  $\text{O}_2\text{CCF}_3$ , CN, and halogen) have quite marked effects on the rates of addition of trifluoroacetic acid to alkenes, the acid acting as both reagent and solvent. The reactions showed pronounced carbonium-ion character. Accordingly, it was of interest to assess the effect of the  $\Delta^1$  double-bond in (+)-(*R*)-limonene. *p*-Menth-8-ene was prepared and its reactivity studied. Table 3 shows that the activation parameters are almost identical and hence no participation occurs.

The reactions were also studied in solvent 1,2-dichloroethane, where dimer formation is minimal [ $K_D$  (25 °C) = 1.5]. A complex kinetic pattern was revealed due to the incursion of an acid-liberating step, possibly as outlined in (6). However, from initial slopes, the early part of the reaction obeys the same kinetic equation as before [equation (1)] as shown in Table 5.

The reaction mixtures were always coloured which

<sup>19</sup> G. Williams and H. Bardsley, *J. Chem. Soc.*, 1952, 1707.

<sup>20</sup> D. P. N. Satchell and J. L. Wardell, *Proc. Chem. Soc.*, 1962, 296.

<sup>21</sup> P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Amer. Chem. Soc.*, 1965, 87, 5163 and preceding papers.

<sup>16</sup> G. Loveluck, *J. Phys. Chem.*, 1960, 64, 385.

<sup>17</sup> R. M. G. Roberts, unpublished work.

<sup>18</sup> D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 1965, 61, 1127.

experience has shown to be characteristic of rearrangement and polymerisation. On removing the solvent from reaction mixtures the residual oils showed a significantly higher refractive index for reaction conducted in more polar solvents such as dichloroethane and nitromethane (1.4377 and 1.4587 respectively) than those in weakly polar solvents like  $\text{CCl}_4$  (1.4224). This

TABLE 5

Variation of initial rates,  $V_0$  ( $\text{mol l}^{-1} \text{s}^{-1}$ ), with concentrations of (+)-(*R*)-limonene (*a*) and trifluoroacetic acid (*b*) for the addition reaction in solvent 1,2-dichloroethane at 25.1 °C

[(+)-( <i>R</i> )-limonene]/M	$[\text{CF}_3\text{CO}_2\text{H}]/\text{M}$	$10^4 V_0$	$10^3 V_0/ab$	$10^2 V_0/ab^2$	$V_0/ab^3$
0.186	0.186	1.6	4.6	2.5	0.13
0.186	0.395	8.4	11.4	2.9	0.07
0.395	0.186	3.7	5.1	2.7	0.15

may well be due to the incursion of a carbonium-ion mechanism and the resultant Wagner–Meerwein shifts and accompanying cationic polymerisation. Similar kinetic behaviour was observed for solvent nitromethane though the rates were somewhat slower.

Brown and Liu<sup>22</sup> have recently investigated the addition of acetic acid and trifluoroacetic acid to norbornene, the acids being employed as the solvents in each case. The additions were characterised by high stereoselectivity to yield the *exo*-esters but when deuteriated acids were used incomplete scrambling of label was observed which argued against a symmetrical carbonium-ion intermediate. The authors reject the possibility of a competitive *cis*-molecular attack on the grounds that for 7,7-dimethylnorbornene such additions, when they occur at all, yield *endo*-products.\* Peterson,<sup>21</sup> in an extended study of additions in solvent trifluoroacetic acid, has demonstrated that the reactions possess a considerable degree of ionic character, which is not surprising for a solvent of such high dielectric constant.  $\Delta H^\ddagger$  Values are considerably larger and  $\Delta S^\ddagger$  values less negative than for the reactions in non-polar media which is generally in keeping with the change from an  $A_{\text{D}}3$  to an ionic mechanism. Unfortunately it is not possible to evaluate the order of reaction with respect to  $\text{CF}_3\text{CO}_2\text{H}$  under these conditions. Systems which have been investigated kinetically in detail include the addition of HCl and HBr to alkenes in solvent acetic acid<sup>2</sup> and in solvent nitromethane.<sup>3</sup> In both cases, the rate was proportional to the square of the acid concentration. The results in acetic acid are interpreted in terms of competitive  $A_{\text{D}}2$  and  $A_{\text{D}}3$  mechanisms for catalysis by HCl whilst catalysis by HBr appears to involve only the latter mechanism. In each case dominant *anti*-addition occurs. This is in marked contrast to similar reactions catalysed by trifluoromethanesulphonic acid<sup>23</sup> which results in a complete

lack of stereospecificity and is characterised by a first-order term in catalyst acid. This behaviour undoubtedly reflects the extremely low nucleophilicity of the  $\text{CF}_3\text{SO}_3^-$  ion and the results seem best interpreted in terms of a rate-determining conversion of an intimate ion-pair to solvent-separated species from which the non-stereospecific products are formed.

The reactions in nitromethane are also accompanied by *anti*-addition *via* apparently a tight-ion paired carbonium-ion intermediate. Whilst it is reasonable to postulate a more ionic mechanism in a more polar solvent such as nitromethane it is difficult to rationalise the high stereospecificity in these terms. In the present study the fact that the polarimetric and titrimetric rate data were comparable argues against an ionic mechanism which would involve hydride shifts. The involvement of a second molecule of HBr in the  $A_{\text{D}}3$  mechanism discussed above is not perhaps surprising in view of the nucleophilicity of the bromine atoms. However, trifluoroacetic acid is much less nucleophilic and its function as a nucleophilic catalyst in this context requires some comment.

From previous studies (+)-(*R*)-limonene has been shown to be more reactive than cyclopentene in addition reactions by a factor of *ca.* 4 000 at 25 °C.<sup>23</sup> A comparison of rate data for the addition of HBr to cyclopentene in acetic acid<sup>7</sup> with that of  $\text{CF}_3\text{CO}_2\text{H}$  addition to (+)-(*R*)-limonene in the present study reveals that  $\text{CF}_3\text{CO}_2\text{H}$  is a less effective reagent by at least a factor of 100.

In summary, the addition of trifluoroacetic acid to (+)-(*R*)-limonene occurs by a mechanism  $A_{\text{D}}3$  involving concerted attack by two molecules of monomer acid in solvent benzene. There is evidence to suggest that in solvent cyclohexane, attack is by the dimeric acid species.

#### EXPERIMENTAL

Solvents cyclohexane, benzene,  $\text{CCl}_4$ , 1,2-dichloroethane, and nitromethane were purified by standard methods. Trifluoroacetic acid was carefully fractionated prior to use. 99.7% atomic %D trifluoroacetic [<sup>2</sup>H]acid was supplied by Koch–Light Laboratories Ltd., or synthesised by careful addition of 99.7 atomic %D  $\text{D}_2\text{O}$  to trifluoroacetic anhydride which gave 95.5% deuterium incorporation.

(+)-(*R*)-Limonene was fractionated under nitrogen. *p*-Menth-8-ene<sup>24</sup> was synthesised by hydrogenating (+)-car-3-ene to give *cis*-(-)-carane which in turn was converted into 8-bromo-*p*-menthane with HBr. Elimination of HBr from the latter with conc. KOH gave a 3 : 1 mixture of *cis*- and *trans*-*p*-menth-8-ene.

Mass spectra were run on an A.E.I. MS12 instrument. <sup>1</sup>H N.m.r. spectra were obtained using a Varian EM-360 instrument (60 MHz). All chemical shifts reported in Hz or  $\delta$  (p.p.m.) from  $\text{SiMe}_4$ .

*Kinetic Technique.*—Solutions of  $\text{CF}_3\text{CO}_2\text{H}$  were made up

<sup>22</sup> H. C. Brown and Kwang-Ting Liu, *J. Amer. Chem. Soc.*, 1975, **97**, 2469.

<sup>23</sup> R. M. G. Roberts, *J.C.S. Perkin II*, 1976, 1183.

\* However Huisgen has recently shown that both diphenylnitrilimine and benzonitrile oxide add to *apo*-norbornene with *exo-cis*-stereospecificity (see W. Fliege and R. Huisgen, *Annalen*, 1973, 2038).

<sup>24</sup> L. Borowiecki, W. Zacharewicz, and J. Przystrupa, *Roczniki Chem.*, 1964, **38**, 1505.

at the desired temperature and allowed to thermally equilibrate for 20 min. The appropriate volume of (+)-(*R*)-limonene was rapidly injected into the acid solution and timing commenced. Aliquots (5 ml) were withdrawn at suitable time intervals and quenched by running into distilled water (25 ml) and titrated against standard alkali using phenolphthalein as indicator. The titration was performed with the tip of the burette close to the surface of the acid solution to avoid entrainment of the added alkali by the upper organic solvent layer. For equimolar solutions  $k_3$  was evaluated by plotting the reciprocal of the square of the titre against time. For other concentrations the more general form of the integrated third-order rate expression was used, shown below, where  $a$  and  $b$  are the olefin and acid concentrations respectively.

Where the reaction was followed by  $^1\text{H}$  n.m.r. spectro-

scopy, aliquots were quenched in an equal volume of  $\text{CCl}_4$  and water. The  $\text{CCl}_4$  layer was separated and dried over magnesium sulphate and the signals due to the olefinic and acid protons were integrated.

$$\frac{1}{b} \left[ \frac{x}{b-x} \right] - \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)} = (a-b)k_3t \quad (7)$$

Activation parameters were calculated in the usual manner and the errors evaluated by a least-squares computer programme.

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