

Hydrogen-bonded complexes of oxetanes and other ethers with nitric acid and with trifluoroacetic acid in $[^2\text{H}]$ trichloromethane†

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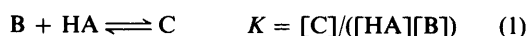
Equilibrium constants for hydrogen-bonded complexation of nitric acid and trifluoroacetic acid with 3,3-pentamethyleneoxetane, oxetane, 3-phenyloxetane, tetrahydrofuran, butyl methyl ether, 3-(4-nitrophenyl)oxetane and dibenzyl ether, measured by ^1H NMR spectroscopy, are reported. Reasons for the signal broadening observed with the more strongly basic ethers with nitric acid but not with trifluoroacetic acid are discussed.

In connection with our studies of the reactions of substituted oxetanes with nitric acid and with dinitrogen pentoxide, on which we shall report later, we describe here a quantitative investigation of the rapid reversible complexation with nitric acid which occurs prior to reaction, as became evident from the observed ^1H NMR chemical shift changes. We examined for comparison similar effects with other cyclic and acyclic ethers, and with trifluoroacetic acid and the same set of ethers.

Previous investigations of hydrogen-bonding equilibria involving nitric acid and ethers appear to be limited to the gas phase.¹ There have been several studies of hydrogen-bonding between trifluoroacetic acid and various ethers in solution, notably aromatic ethers in trichloromethane.² Hydrogen-bonded self-association of trifluoroacetic acid must also be considered in any quantitative investigation. The formation constant for the dimer (probably cyclic³) of this acid is reported to be strongly dependent on the solvent; values range from $320 \text{ dm}^3 \text{ mol}^{-1}$ in cyclohexane to $1.5 \text{ dm}^3 \text{ mol}^{-1}$ in dichloroethane.³ Hydrogen bonded self-association of nitric acid in trichloromethane is clearly also a possibility, but this does not appear to have been investigated previously. Possible dimerisation of the acids is taken into account in our studies, on which we now report.

Results

The ^1H chemical shifts of the proton signals α to the oxygen in each of the ethers all increased with the concentration of the added acid. These are illustrated in Fig. 1, and demonstrate that such shifts approach a limiting value at high concentrations. The shifts are greater for the protons nearest to the basic centre, and the fact that, for instance the γ and δ proton signals of the butyl group of butyl methyl ether are shifted by less than 4 Hz, whereas the α proton signal is shifted by 79 Hz, clearly indicates that changes in solvent susceptibility due to addition of the acid contribute little to the observed effect. Shifts which are larger by *ca.* 25 Hz, after correction for solvent effects, are observed on protonation (as observed when the ethers are dissolved in trifluoroacetic acid) and the simplest reasonable interpretation of the present results is that the shifts are not due to protonation but to hydrogen-bonded complex formation between the ether, B, and the acid, HA, to form a 1:1 complex, C, [eqn. (1)] in an



equilibrium which relaxes rapidly on the NMR time-scale. If self-association of the acid to form a dimer, D, is also

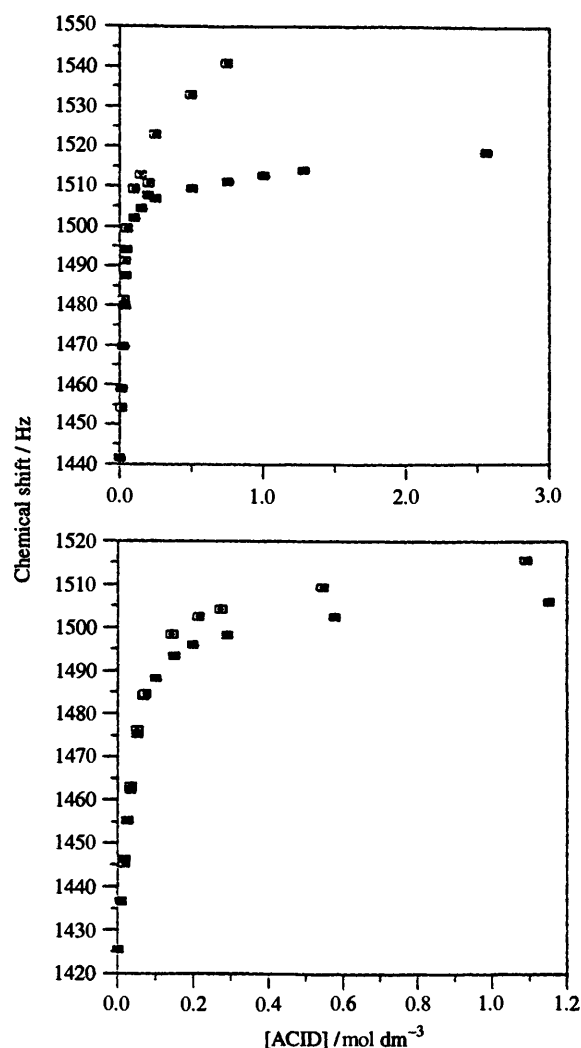
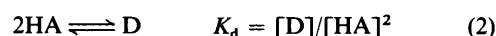


Fig. 1 A plot of the change in chemical shift of a methylene proton of 3-phenyloxetane (top) and of 3-(4-nitrophenyl)oxetane (bottom) with increasing concentration of TFA (closed symbols) or nitric acid (open symbols) in $[^2\text{H}]$ trichloromethane at 30°C

important, then the equilibrium of eqn. (2) must be taken into



account. If the total concentrations of acid and ether are *a* and *b*, respectively, eqns. (3) and (4) follow from the stoichiometry.

$$a = [\text{HA}] + 2[\text{D}] + [\text{C}] \quad (3)$$

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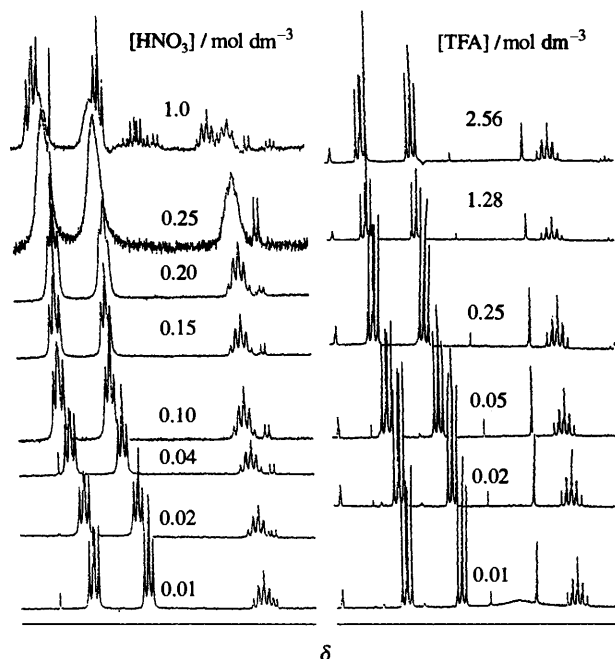


Fig. 2 The effect of change in concentration of nitric acid (left) and TFA (right) on the ^1H NMR spectrum of 3-phenyloxetane at 30 °C. The spectrum at $[\text{HNO}_3] = 1.0 \text{ mol dm}^{-3}$ shows sharp product peaks and broad 3-phenyloxetane peaks.

$$b = [\text{B}] + [\text{C}] \quad (4)$$

Eqns. (1)–(4) can be combined to give the following relation [eqn. (5)] in which the only unknown concentration is $[\text{HA}]$.

$$a = [\text{HA}] + 2K_d[\text{HA}]^2 + bK[\text{HA}]/(1 + K[\text{HA}]) \quad (5)$$

The calculated chemical shift δ of a proton signal from the ether is given by eqn. (6), in which F is the fraction of the ether which

$$\delta = FU + (1 - F)V \quad (6)$$

is free $\{F = 1/(1 + K[\text{HA}])\}$, and U and V are the chemical shifts of a particular proton signal in the free and complexed ether, B and C, respectively.

The simplifying assumptions were made that the equilibrium constants K and K_d , and the chemical shifts U and V , are medium-independent over the range of acid concentrations (0.02–0.5 mol dm $^{-3}$) considered. The chemical shift U can be measured directly, in the absence of acid, but the limiting value V of the chemical shift at high concentrations of acid is approached but not reached, as is illustrated in Fig. 1. Eqn. (5) provides a quadratic expression in $[\text{HA}]$ which can be solved for a range of assumed values of K . Each leads to a best-fitting value of V by the principle of least squares [eqn. (6a)]. Values of

$$V = \{\Sigma[\delta_{\text{obs}}(1 - F)] - U\Sigma[F(1 - F)]\}/\Sigma[(1 - F)^2] \quad (6a)$$

K and V were thus chosen to minimise the sum of the squares of the differences between calculated and observed chemical shifts, $\Sigma(\delta - \delta_{\text{obs}})^2$.

In this process a value of K_d was assumed for all equilibria relating to a particular acid. It was found that the best global minima were achieved with $K_d = 2 \text{ dm}^3 \text{ mol}^{-1}$ for nitric acid and $K_d = 13 \text{ dm}^3 \text{ mol}^{-1}$ for trifluoroacetic acid, and these are the values which were used in the calculations reported below. It is stressed, however, that the results were rather insensitive to the value of K_d used. Any value between 1 and 5 dm $^3 \text{ mol}^{-1}$ for nitric acid and between 10 and 25 dm $^3 \text{ mol}^{-1}$ for trifluoroacetic acid would be satisfactory. This is not a practicable way to

Table 1 Equilibrium constants K for hydrogen-bonded complex formation^a in $[\text{^2H}]\text{-CHCl}_3$

Ether	Trifluoroacetic acid ^b		Nitric acid ^c	
	$K/\text{dm}^3 \text{ mol}^{-1}$	rms ^d /Hz	$K/\text{dm}^3 \text{ mol}^{-1}$	rms ^d /Hz
3,3-Pentamethyleneoxetane	218	0.5		
Oxetane	204	0.8		
3-Phenyloxetane	180, 163	0.6, 0.6		
Tetrahydrofuran	153	0.7	103 ^e	1.1
Butyl methyl ether	160, 152	0.3, 0.6	96 ^e , 96 ^e	1.0, 0.7
3-(4-Nitrophenyl)oxetane	72, 63	0.9, 0.6	51, 46	0.6, 0.6
Dibenzyl ether	25	0.3	17	0.6

^a See eqn. (1). Where two values are given these relate to measurements based on the two α -proton signals of the ether. Errors in K estimated as $\pm 10\%$ except where stated. ^b Assuming $K_d = 13 \text{ dm}^3 \text{ mol}^{-1}$ [see eqn. (2)]. ^c Assuming $K_d = 2 \text{ dm}^3 \text{ mol}^{-1}$ [see eqn. (2)]. ^d The root mean square (rms) of the differences between calculated and observed chemical shifts, in Hz, for 7–9 points over the range of acid concentrations 0.02–0.50 mol dm $^{-3}$. Total shifts $V - U$ [see eqn. (6)] were in the range 40–90 Hz. ^e $\pm 15\%$.

Table 2 Observed (δ_{obs}) and calculated (δ) chemical shifts (in Hz) for the two α -proton signals (α_a and α_b) of 3-phenyloxetane (0.04 mol dm $^{-3}$) with various concentrations, a , of trifluoroacetic acid in $[\text{^2H}]\text{-trichloromethane}$

$a/\text{mol dm}^{-3}$	α_a -proton signal		α_b -proton signal	
	δ_{obs}	$\delta(\text{for } K = 180 \text{ dm}^3 \text{ mol}^{-1})^a$	δ_{obs}	$\delta(\text{for } K = 163 \text{ dm}^3 \text{ mol}^{-1})^a$
0	$U = 1441.4$		$U = 1527.5$	
0.02	1469.6	1469.6	1551.6	1551.7
0.03	1479.9	1480.3	1560.4	1560.7
0.04	1487.6	1487.9	1567.0	1567.3
0.05	1494.1	1493.0	1572.7	1571.7
0.10	1502.0	1502.3	1579.8	1580.0
0.15	1504.4	1505.0	1582.0	1582.5
0.25	1506.9	1507.1	1584.1	1584.5
0.50	1509.5	1508.9	1586.9	1586.2
	$V = 1512.1^a$		$V = 1589.3^a$	

^a Best-fitting values.

measure K_d and these values should be treated with caution. Our interest was in the constants K and fortunately the choice of the value of K_d within the limits quoted made only small differences to the estimated values of K reported below. Though imprecise in this respect, the results indicate significant self-association of both acids under the conditions.

Signals for protons on carbon atoms attached to the oxygen of the ether were used. Where two such signals were available, estimated values of K from each were in reasonable agreement given the assumptions referred to above. The procedure described gave satisfactory fits for all the trifluoroacetic acid results, and (with somewhat larger errors) for the four most weakly basic ethers with nitric acid. The results are shown in Table 1. (Ethers are listed in order of decreasing measured hydrogen-bonding basicity.) An example of a set of observed and calculated shifts is given in Table 2.

The chemical shift changes observed for the more strongly basic ethers with nitric acid were very similar to those observed with trifluoroacetic acid at low acid concentrations, but at higher acid concentrations there was considerable broadening of the signals. This is illustrated for 3-phenyloxetane in Fig. 2. It prevented a reliable estimate of K in these cases. Slight broadening was detected also with butyl methyl ether and tetrahydrofuran which contributes to the larger errors in these cases (Table 1). The broadening is discussed further below.

Discussion

Hydrogen-bonding basicities and acidities

The ratio of values of K for the two acids (trifluoroacetic and nitric) for the four ethers for which comparison can be made, all fall in the range 1.4–1.6 (Table 1). Trifluoroacetic acid is thus the stronger hydrogen bonding acid, under these conditions. Their relative Brønsted acidities are in the opposite order. (Values of pK_a of -2.2 for nitric acid^{4a} and -0.6 for trifluoroacetic acid^{4b} have been reported.) With regard to the relative hydrogen-bond basicities of the ethers, there appear to have been no studies with such strong acids as used here. A comprehensive compilation⁵ of hydrogen-bond strengths lists values of $K/\text{dm}^3 \text{ mol}^{-1}$ for complexes with a number of acids, of which those for phenol in tetrachloromethane at 25 °C of oxetane, tetrahydrofuran, diethyl ether (presumably very similar to butyl methyl ether) and dibenzyl ether of 16, 16, 8.9 and 3.7, respectively, allow the closest comparison with the present work. Our results in contrast show that, towards trifluoroacetic acid, oxetane is a significantly stronger hydrogen-bonding base than is tetrahydrofuran.

Substituent effects in the oxetane series are in the direction expected; 3,3-pentamethyleneoxetane is of similar basicity to the parent oxetane, and 3-phenyloxetane rather weaker, reflecting the inductive electron withdrawal of the phenyl ring. 3-(4-Nitrophenyl)oxetane is a markedly weaker hydrogen bonding base than 3-phenyloxetane.

NMR line broadening

Fig. 2 illustrates the NMR line broadening. This is not due to a reduction in the rate of conformational change in the oxetane ring caused by complexation, because there was no detectable broadening in the case of 3-(4-nitrophenyl)oxetane. Broadening was in any case not restricted to oxetanes; it was detectable with tetrahydrofuran and with butyl methyl ether. We briefly considered the possibility that microheterogeneity was setting in with high concentrations of nitric acid. However this hypothesis can be rejected because for the two weakest ethers there was no sign of line broadening even at nitric acid concentrations as high as 1 mol dm^{-3} .

Any explanation must account for the facts that the broadening was observed only for the more strongly basic ethers, only at high concentrations of nitric acid and not with trifluoroacetic acid at any concentration. The ether was regenerated on quenching and the observations are quite distinct from the slow irreversible ring opening reaction which will be described in a later publication and which is signalled in the additional sharp peaks beginning to appear in the spectrum for the highest nitric acid concentration in Fig. 2. At first, the most obvious explanation appeared to be that an equilibrium extent of protonation is occurring [eqn. (7)], in which B·HA is



the hydrogen-bonded complex called C above and $\text{BH}^+ \text{A}^-$ is the ion pair). This would be expected to be most manifest with the more basic ethers and with the stronger Brønsted acid (*i.e.* nitric acid), as observed. That the hydrogen bonded complex is persuaded to transfer its proton only at high concentrations of acid could be accounted for by the need for hydrogen-bonded solvation of the formed anion. (Quantitative analysis based on this idea was attempted, but did not prove to be useful because of the unavoidable increase in the number of fitting parameters.) The major difficulty with this interpretation is that proton transfer equilibria between oxygen centres would not be expected to be slow on the NMR time-scale; sharp time-averaged spectra would be anticipated.

An alternative explanation is that there is present, at high concentrations of nitric acid and with the more strongly basic ethers, a small equilibrium concentration of the ether-

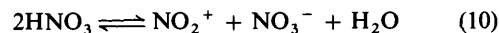
nitronium ion complex [reaction (8)]. We have attempted to



investigate reaction (8) independently, using nitronium trifluoromethanesulfonate. The insolubility of the latter in trichloromethane precluded a complete study, but clear evidence of complexation was obtained from the shift in the ether proton signals, which were sharp (see Experimental section). Thus the equilibria (8) and (9) exist. They are linked



through the equilibrium in reaction (10) and if this relaxes



relatively slowly this may account for the broadening. Our preferred explanation for the broadening is therefore based on the linked equilibria of reactions (8)–(10).

An investigation of the effect of temperature on the ^1H NMR spectrum of 3-phenyloxetane in $[\text{2H}]$ trichloromethane containing 0.35 mol dm^{-3} HNO_3 showed that there was further broadening up to 40 °C but sharp signals were restored at -20 °C without new signals appearing. This is consistent with the above interpretation if the equilibrium extent of nitronium complex formation is small at low temperatures. It is interesting that, as we shall report elsewhere, the ether-nitronium ion complexes of oxetanes are probably intermediates in their ring-opening reactions engendered by nitric acid, rather than the protonated oxetanes, because the dinitrate products are formed directly and not *via* mononitrates.

Experimental

Apparatus

All ^1H NMR spectra were recorded on a 300 MHz Bruker Spectrometer. J values are given in Hz.

Materials

Chemicals were used as supplied unless otherwise stated. 1,1-Bis(hydroxymethyl)cyclohexane and 3,3-pentamethyleneoxetane were kindly provided by Dr John Dormer, who prepared them as described.⁶ $[\text{2H}]$ Trichloromethane and tetrahydrofuran were dried by distillation in silanized glassware over calcium hydride immediately before use.

Preparation of 2-phenylpropane-1,3-diol

To a solution of lithium aluminium hydride (7.20 g, 0.163 mol) in anhydrous THF (120 ml) was added a solution of phenylmalonic acid (9.00 g, 0.05 mol), also in anhydrous THF (40 ml), over a period of 20 min allowing gentle reflux to occur. The grey solution was then heated to reflux for a further 30 min, during which period the solution changed to a dirty lime green colour. The reaction mixture was cooled in an ice-bath for 30 min after which a solution of water and THF (1:4, 50 ml) was cautiously added over a period of 40 min causing further reflux. The mixture was refluxed for a further 30 min after which only white solid remained in the yellow solution. After cooling in an ice-bath, 10% aqueous sulfuric acid (100 ml) was added to the reaction mixture with stirring over a period of 10 min. The solution rapidly turned light green and separated into two layers, the lower one containing a thick white precipitate (flame-test indicates lithium salt). The reaction mixture was added to a 1 l separating funnel and diluted with dichloromethane (DCM, 200 ml) and water (200 ml). The organic layer was separated and the aqueous layer extracted further using DCM (4×100 ml). The combined organic extracts were dried over anhydrous magnesium sulfate for 24 h. After filtration the solvent was evaporated to yield a clear yellow oil (4.60 g) as crude product. This was purified by vacuum distillation.

The first fraction, a clear colourless liquid (0.69 g), was collected over a temperature range (66–68 °C mmHg). This was identified as a mixture of (a) 2-phenylethanol (79%) and (b) 2-phenylpropan-1-ol (21%). δ_{H} (300 MHz; CDCl_3) 1.29 [3 H, d, J 7.63, C-3 methyl (b)], 1.76 [1 H, br s, hydroxy (a and b)], 2.87 [2 H, t, J 6.61, C-1 methylene (a)], 2.95 [1 H, q, C-2 methine (b)], 3.70 [2 H, d, J 6.72, C-1 methylene (b)], 3.85 [2 H, t, C-1 methylene (a)], 7.22–7.35 [5 H, m, aromatic (a and b)]; δ_{C} (75.47 MHz; CDCl_3) 17.597 [C-3 methyl (b)], 39.21 [C-1 methylene (a)], 42.445 [C-2 methine (b)], 63.638 [C-2 methylene (a)], 68.671 [C-1 methylene (b)], 126.098, 126.652, 127.490 [aromatic C-H (b)], 143.748 [aromatic C (b)], 126.456, 128.621, 129.033 [aromatic C-H (a)], 138.551 [aromatic C (a)].

The second fraction also a clear colourless oil (0.08 g) (bp 68–100 °C 0.05 mmHg) which was also identified by ^1H NMR spectroscopy as being a mixture of 2-phenylethanol (71%) and 2-phenylpropan-1-ol (29%).

The third fraction (bp 106–108 °C 0.01 mmHg) a pale yellow oil (2.48 g, 13.1 mmol, 33.0%), was identified as the expected diol product. ν_{max} (oil/ cm^{-1}) 3374 (m, simple H-bonded OH), 1026 (s, C–O), 759, 701 (s, 5 adjacent aromatic C–H); δ_{H} (300 MHz; CDCl_3) 3.05 (1 H, quintet, C-2 methine), 3.5–3.9 (2 H, br s, 2 \times hydroxy), 3.95 (4 H, m, C-1 and C-3 methylenes), 7.1–7.35 (5 H, m, aromatic); δ_{C} (75.47 MHz; CDCl_3) 49.71 (methine C-2), 65.69 (C-1 and C-3 methylenes), 127.21, 128.03, 128.80 (C–H aromatic), *ca.* 140 (C aromatic); m/z (M^+ , 152.084 14, required M , 152.083 730, dev. 2.7 ppm) (Found: C, 71.10; H, 7.93. Calc for $\text{C}_9\text{H}_{12}\text{O}_2$: C, 71.01; H, 7.95%).

Preparation of 3-phenyloxetane

This was prepared from 2-phenylpropane-1,3-diol as described previously.⁷ The crude product was purified by vacuum distillation (bp 32–34 °C 0.02 mmHg) to give a clear colourless oil (1.16 g, 8.64 mmol, 31.4%). R_f (0.30; 100% DCM; silica); ν_{max} (oil/ cm^{-1}) 3063 (w, C–H str.), 3031, 2963, 2874 (m, CH_2 str.), 982 (s, oxetane), 756, 699 (s, 5 adjacent arom. unsubstituted); δ_{H} (300 MHz; CDCl_3) 4.24 (1 H, m, C-2 methine), 4.80 (2 H, t, methylene), 5.10 (2 H, q, methylene), 7.3–7.5 (5 H, aromatic); δ_{C} (75.47 MHz; CDCl_3) 40.370 (C-2 methine), 78.861 (C-1 and C-3 methylenes), 126.791, 127.027, 128.764 (aromatic C–H), 141.576 (aromatic C–); m/z (M^+ 134.0723, required M 134.073 165, dev. –3.2 ppm).

Preparation of 3-(4-nitrophenyl)oxetane

To dinitrogen pentoxide (1.89 g, 17.5 mmol) in dry DCM (40 ml) at 0 °C was added a solution of 3-phenyloxetane (0.241 g, 1.80 mmol), in dry DCM also at 0 °C. The reaction mixture was allowed to stand in an ice-bath for 5 min after which it was rapidly quenched in an excess of ice-cold aqueous sodium hydrogen carbonate. The organic layer was removed and the aqueous layer extracted by DCM (3 \times 50 ml). The DCM fractions were combined and dried over anhydrous magnesium sulfate for 24 h. After filtration the solvent was evaporated to give a yellow oil as crude product. This was purified by column chromatography over silica to give the desired product in yield (>80%), mp 59.0–60.0 °C; ν_{max} (solution; DCM)/ cm^{-1} 1518 (m, asym. str. C–NO₂), 147 (m, sym. str. C–NO₂), 982 (mw, oxetane); δ_{H} (300 MHz; CDCl_3) 4.31 (1 H, m, C-2 methine), 4.74 (2 H, t, J 6.22, C-1/C-3 methylene protons), 5.14 (2 H, q, C-1/C-3 methylene protons), 7.55 (2 H, dt, aromatic *para*-substitution), 8.25 (2 H, dt, aromatic *para*-substitution); m/z (M^+ , 179.059 18, $\text{C}_9\text{H}_9\text{NO}_3$ requires M , 179.058 243, dev. –5.2% ppm) (Found: C, 59.82; H, 5.17; N, 7.48. $\text{C}_9\text{H}_9\text{NO}_3$ requires: C, 60.33; H, 5.06; N, 7.82%).

A small amount (*ca.* 5%) of 2-(2-nitrophenyl)propane-1,3-diyl dinitrate was also recovered. δ_{H} (300 MHz; CDCl_3) 4.15 (1 H, quintet, methine), 4.75–4.9 (4 H, m, C-1/C-3 methylenes), 7.6–8.0 (4 H, m, aromatic *ortho*-substitution).

Preparation of anhydrous trifluoroacetic acid

To a 100 ml flask was added 20 ml of 100% sulfuric acid. The solution was cooled in an ice-bath and trifluoroacetic acid (50 ml) was cautiously added. The trifluoroacetic acid was distilled from the sulfuric acid while under a nitrogen atmosphere, the first 10 to 15% being discarded.

Preparation of dinitrogen pentoxide

This was prepared as previously described.⁸

Preparation of nitronium trifluoromethanesulfonate

To trifluoromethanesulfonic acid (0.5 g, 3.33 mmol) was added an excess of dinitrogen pentoxide in dichloromethane. White crystals formed. Solvent, nitric acid and remaining dinitrogen pentoxide were removed under high vacuum to leave white crystals of nitronium trifluoromethanesulfonate. A saturated solution of this salt in [^2H]trichloromethane was prepared. Titration revealed that the concentration of the saturated solution was 6.5×10^{-3} mol dm^{-3} .

Preparation of anhydrous nitric acid

Concentrated sulfuric acid (150 ml) was added to a long necked 500 ml flask with an inverted ground glass joint and was then cooled in an ice-water bath. Fuming nitric acid (70 ml) was slowly added to the sulfuric acid, resulting in a clear, colourless solution. The ice-water bath was replaced by liquid nitrogen, freezing the acid mixture. The apparatus was placed under vacuum and then sealed. The mixed acid was freeze-thawed three times to remove volatile impurities by placing one collecting tube in liquid nitrogen while gradually allowing the solid to melt and warm slightly. The anhydrous nitric acid was then vacuum distilled into the liquid nitrogen immersed second flask with gentle warming of the acid mixture.

Complexation of ethers with anhydrous nitric acid and trifluoroacetic acid in [^2H]trichloromethane at 30 °C

To a 5 mm NMR tube was added a known volume of dried substrate in dry CDCl_3 , such that when made up to 500 μl the solution had a substrate concentration of 0.040 mol dm^{-3} . A combination of freshly distilled CDCl_3 and either anhydrous TFA or anhydrous nitric acid in dry CDCl_3 was then added to the substrate solution giving a total solution volume of 500 μl . A wide range of acid concentrations were examined for each substrate. ^1H NMR spectra of these solutions were then obtained at a temperature of 30 °C.

Complexation of 3-phenyloxetane with nitric acid over a temperature range

A solution of 3-phenyloxetane (0.040 mol dm^{-3}) and anhydrous nitric acid (0.35 mol dm^{-3}) in CDCl_3 of total volume 500 μl was made up in a 5 mm NMR tube. The ^1H NMR spectra for this solution were obtained at 10 °C intervals over the temperature range –60 °C to 60 °C.

Complexation of 3,3-pentamethyleneoxetane with nitronium ion

The oxetane ring protons of 3,3-pentamethyleneoxetane (concentration, first figure) in [^2H]trichloromethane solutions containing nitronium trifluoromethanesulfonate (concentration, second figure) were found to give sharp, unbroadened signals with chemical shifts at 300 MHz (third figure) as follows: 0.04 mol dm^{-3} , 0 mol dm^{-3} , 1310.77 Hz; 0.04 mol dm^{-3} , 0.0046 mol dm^{-3} , 1323.94 Hz; 0.00536 mol dm^{-3} , 0.0063 mol dm^{-3} , 1380.00 Hz; 0.00268 mol dm^{-3} , 0.0064 mol dm^{-3} , 1400.20 Hz.

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