Nitrosation of Acetylacetone (Pentane-2,4-dione) and some of its Fluorinated Derivatives

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Nitrosation of acetylacetone (AA) (pentane-2,4-dione), 1,1,1-trifluoropentane-2,4-dione (TFA), and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (HFA) occurs readily in acetonitrile using t-butyl nitrite under mildly acidic conditions. In this solvent the reactants exist primarily in their enol forms and the equilibrium constants K_E have been estimated using ^1H n.m.r. Kinetic studies at different acidities show that whilst AA reacts entirely *via* the enol form, TFA reacts *via* both the enol and enolate forms and HFA reacts only *via* the enolate anion. The results demonstrate both the deactivating effect of the CF_3 group to electrophilic addition and also its acid strengthening effect. In all cases the rate-limiting step is the reaction of the nitrosating agent (probably NO^+) with the enol or enolate. Similar results are reported for the reaction of TFA in dilute aqueous acid using nitrous acid, and also for the reactions catalysed by Cl^-, Br^-, and SCN^-; again reactions occur simultaneously by way of the enol and enolate forms.

In a recent paper[1] we presented the results of a kinetic study of the nitrosation of ketones in aqueous acid solution for ketones which exist predominantly in their keto forms. The results show that the mechanism involves electrophilic attack by a carrier of NO^+ at the enol form of the ketone. For two simple ketones (acetone and butan-2-one) either the attack by the nitrosating agent, or the enolisation of the ketone can be made rate limiting depending upon the experimental conditions. The rate constants measured for enolisation (when there is a zero-order kinetic dependence upon $[HNO_2]$) were identical, within experimental error, with those measured in the classical halogenation (and other) reactions of ketones. We were unable to achieve rate-limiting enolisation of acetylacetone (AA) no doubt due to the higher [enol], and the powerful electron-withdrawing effect of the $COCH_3$ group. Another study[2] showed that dimedone (5,5-dimethyl-1,3-cyclohexanedione) (93% enol in aqueous solution) reacts partly *via* the enol and partly *via* the enolate, in a proportion which is dependent on the acidity of the medium. We have now extended this work to examine the generality of the involvement of the enolate in these reactions. We chose to examine the results of the powerful electron-withdrawing effect of the CF_3 group, and now report the results of the nitrosation kinetics of AA, and the two fluorinated derivatives, 1,1,1-trifluoropentane-2,4-dione (TFA) and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (HFA). Nitrosation was brought about using t-butyl nitrite

$CH_3COCH_2COCH_3$
AA

$CF_3COCH_2COCH_3$
TFA

$CF_3COCH_2COCF_3$
HFA

(TBN) in acetonitrile and also using nitrous acid in water. These two solvents represent limiting cases where the extent of enolisation is (*a*) very large and (*b*) very small, respectively. Recent work[3] has shown that in acetonitrile reaction of alkyl nitriles (and nitrous acid) with very reactive substrates such as thiols and alcohols, occurs by rate-limiting NO^+ formation, whereas for less reactive substrates the rate-limiting step is attack by NO^+.

Experimental

AA was purified by distillation; commercial samples of TFA and HFA were used without further purification. The alkyl nitrites TBN and isopropyl nitrite were prepared by the standard procedure[4] of nitrosation of the corresponding alcohol, and fresh solutions were made up frequently. Sodium nitrite solutions were made up daily. Acetonitrile (HPLC grade) was refluxed with calcium hydride and fractionally distilled from calcium hydride. Rate measurements were carried out at 25 °C, spectrophotometrically, either by the stopped-flow technique or in a conventional recording spectrophotometer, usually by noting the decreasing absorbance due to nitrous acid or the alkyl nitrite at *ca.* 380 nm or in some cases additionally by noting the increasing product absorption at around 220 nm. Both procedures gave similar results within the experimental errors. Experiments were carried out under first-order conditions with $[\text{ketone}] \gg [\text{RONO}]$ or $[HNO_2]$, and good first-order behaviour was found throughout, except where noted with some experiments with isopropyl nitrite. The expected oxime $CH_3COC(=NOH)COCH_3$ was recovered from the reaction of AA with TBN in acetonitrile and was shown to be identical (by u.v. and i.r. spectroscopy) with the oxime recovered from the corresponding reaction with nitrous acid in water. The oximes from the reactions of TFA and HFA decomposed during isolation. There is no reference to these products in the literature. However, the products were stable in solution and their u.v. spectra were very similar to that obtained from AA. Further ^1H n.m.r. experiments in CD_3CN and $CDCl_3$ for both TFA and HFA reactions were totally consistent with oxime formation. In particular the signals due to the C–H and O–H protons disappeared upon reaction and a new signal appeared consistent with the =N–OH protons (Table 1).

Results and Discussion

(a) *Reactions with t-Butyl Nitrite* (*TBN*) *in Acetonitrile.*—All three substrates were examined by ^1H n.m.r. to establish the keto:enol ratio. The chemical shifts, assignments, and relative intensities are given in Table 2. AA was found to be 67% in the

Table 1. ^1H N.m.r. data for TFA and its nitrosation product in $CDCl_3$.

TFA		Product	
δ/ppm	assignment	δ/ppm	assignment
2.13	CH_3	2.36	CH_3
5.86	CH		
14.23	OH	11.76	=N–OH

Table 2. ^1H N.m.r. data for AA, TFA, and HFA in CD_3CN.

	δ/ppm	Relative intensity	Assignment
AA	1.58	6.0	CH_3 enol
	1.76	3.0	CH_3 keto
	3.18	1.0	CH_2 keto
	5.16	1.0	CH enol
TFA	1.83	3.0	CH_3 enol
	5.63	1.0	CH enol
	13.88	1.0	OH enol
HFA	2.85	trace only	CH_2 keto
	6.10		CH enol

Table 3. First-order rate constants for the nitrosation of AA by TBN (1×10^{-3} mol dm^{-3}) in acetonitrile.

(*a*) $[H_2SO_4] = 4.44 \times 10^{-3}$ mol dm^{-3}		(*b*) $[AA] = 1.61 \times 10^{-2}$ mol dm^{-3}	
[AA]/ mol dm^{-3}	k_0/s^{-1}	$[H_2SO_4]$/ mol dm^{-3}	k_0/s^{-1}
0.0202	0.922 ± 0.029	0.0117	3.94 ± 0.14
0.0808	2.21 ± 0.04	0.0234	10.4 ± 0.3
0.143	5.07 ± 0.19	0.0351	16.6 ± 0.6
0.287	10.9 ± 0.1	0.0468	22.3 ± 2.1
0.430	14.4 ± 0.4	0.0585	31.6 ± 1.3

Table 4. Effect of added t-butyl alcohol in the nitrosation of AA by TBN in acetonitrile.

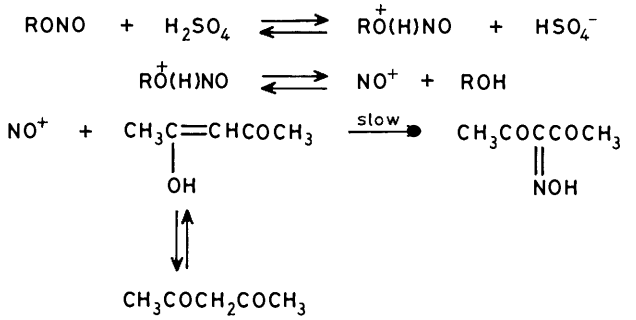
(*a*) At low [acid]^a		(*b*) At higher [acid]^b	
[Bu^{t}OH]/ mol dm^{-3}	$10^3\ k_0$/s^{-1}	[Bu^{t}OH]/ mol dm^{-3}	k_0/s^{-1}
0	37.3 ± 4.4	0	4.41 ± 0.24
0.0205	4.13 ± 0.32	0.0053	1.30 ± 0.09
0.0410	2.43 ± 0.32	0.0158	0.21 ± 0.03
		0.0316	0.115 ± 0.006

^{a} $[H_2SO_4] = 9.0 \times 10^{-4}$ mol dm^{-3}, [AA] = 0.0314 mol dm^{-3}. ^{b} $[H_2SO_4] = 3.5 \times 10^{-2}$ mol dm^{-3}, [AA] = 9.64×10^{-3} mol dm^{-3}.

enol form, *i.e.* giving a K_E value of 2.0, whereas both TFA and HFA are overwhelmingly present as the enol forms. We find only trace amounts of the keto isomers and estimate that in both cases the enol content is not less than 97%. Similar results have previously been obtained in other aprotic solvents such as $CDCl_3$ and $(CD_3)_2SO$, and the signal assignments and chemical shifts[5] are comparable with ours. In general enol content is much higher in non-polar solvents than for example in water, resulting it is thought from the stabilisation of the keto form in polar solvents.[6]

Kinetically the reaction with AA is first-order in both [TBN] and [AA] and although the reaction is clearly acid catalysed, k_0 (the first-order rate constant) is not a linear function of $[H_2SO_4]$. The data are given in Table 3. The 'acidity' cannot therefore be described by the stoicheiometric concentration of sulphuric acid. It is important to note, however, that there is no evidence of a significant intercept at $[H_2SO_4] = 0$. The reaction rate is much inhibited by the addition of t-butyl alcohol. The data in Table 4 show the values of k_0 as a function of added [Bu^{t}OH] for two different acidities.

The results suggest a mechanism in which a nitrosating agent is reversibly and rapidly formed, which then reacts in the rate-limiting step with the enol form of AA. The most likely nitrosating species in this solvent is the nitrosonium ion NO^+, given the earlier work with the more reactive substrates,[3] and also the pronounced retardation on Bu^{t}OH addition. The sequence is set out for a general alkyl nitrite RONO in Scheme 1. We have written, for convenience, the nitrosation stage as one step, but clearly it involves electrophilic addition, followed by rapid proton loss and tautomeric shift to the oxime. We can obtain an approximate value for k_1 the third-order rate constant for reaction with the enol (defined by rate = $k_1[RONO][AA][H_2SO_4]$), at $[H_2SO_4] = 0$, as *ca.* 3×10^4 dm^6 mol^{-2} s^{-1}. We cannot be more precise, since the plot of k_0 *vs.* $[H_2SO_4]$ is a slight upward curve.



$$RONO + H_2SO_4 \rightleftharpoons RO\overset{+}{(H)}NO + HSO_4^-$$

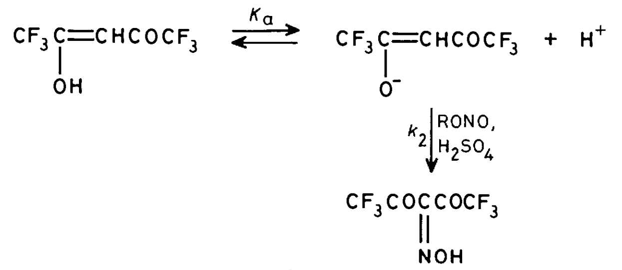
$$RO\overset{+}{(H)}NO \rightleftharpoons NO^+ + ROH$$

$$NO^+ + CH_3\underset{OH}{C}{=}CHCOCH_3 \xrightarrow{slow} CH_3CO\underset{NOH}{\overset{}{C}}COCH_3$$

$$CH_3\underset{OH}{C}{=}CHCOCH_3 \rightleftharpoons CH_3COCH_2COCH_3$$

Scheme 1.

Similar spectral behaviour is found for the reaction of HFA with TBN in acetonitrile. The n.m.r. signal at δ 6.10 ppm (CH enol) disappeared upon reaction. The kinetic results are reported in Table 5 and show clearly that the reaction is first order with respect to [HFA] but now zero order in $[H_2SO_4]$ over a tenfold range of concentration. The results in Table 5 are from kinetic measurements of the disappearance of TBN at 380 nm, similar results were obtained at a different [HFA] measuring the appearance of product at 220 nm. The results suggest strongly that reaction now occurs exclusively *via* the enolate ion (see Scheme 2). In effect now the acid catalysis necessary for NO^+ generation is offset by protonation of the enolate to give in this case a totally unreactive enol. It is to be expected that this enol would be many orders of magnitude less reactive to electrophilic addition than that derived from AA, because of the very powerful influence of the CF_3 groups. The pK_a of the enol in acetonitrile is not known, but in water this enol is quite acidic (pK_a 4.71).[7] The measured first-order rate constant k_0 is then given by k_2K_a[HFA], where k_2 is the third-order rate constant for reaction of the enolate and K_a the acid dissociation constant of the enol. From the four sets of results (two of which



$$CF_3\underset{OH}{C}{=}CHCOCF_3 \overset{K_a}{\rightleftharpoons} CF_3\underset{O^-}{C}{=}CHCOCF_3 + H^+$$

$$CF_3\underset{O^-}{C}{=}CHCOCF_3 \xrightarrow[k_2]{RONO,\ H_2SO_4} CF_3CO\underset{NOH}{C}COCF_3$$

Scheme 2.

are shown in Table 5) we get values of k_2K_a of 39 ± 1, 36 ± 4, 36 ± 5, and 33 ± 2 $dm^3 mol^{-1} s^{-1}$, which are in good agreement.

Reaction also occurred readily with the trifluoro derivative TFA and again all the spectral data are consistent with oxime formation. The results are given in Table 6. As for the other reactants reaction is strictly first order in [TFA], but although reaction is acid catalysed, the dependence is now different from that for [AA] in that there is a significant positive intercept to the plot of k_0 *vs.* [H_2SO_4]. Similar results (not shown) were obtained for the acid catalysis at another [TFA]. These results are readily interpreted in terms of simultaneous reaction of the enol and enolate derived from TFA. Similar behaviour has been noted earlier[8] when both benzenesulphinic acid and the benzenesulphinate anion are reactive in nitrosation; in the same way the enol and enolate derived from dimedone are both reactive.[2] In both cases this is deduced from plots of k_0 *vs.* the acidity which are linear with substantial positive intercepts.

The pK_a values in water are reported as 6.7,[9] 6.56[10] (TFA), 8.87,[11] 9.05[10] (AA) and 4.71[7] (HFA), so if the trend is repeated in acetonitrile solvent, then it is not surprising that the pattern of behaviour of TFA lies between that of AA and HFA. In principle we can obtain k_1 (the third-order rate constant for reaction of the enol form) from the kinetic results, but since k_0 *vs.* [H_2SO_4] are not strictly linear (for AA and TFA) this is not possible with accuracy. However, we can estimate (at [H_2SO_4] = 0) a value of k_1 for TFA of *ca.* 800 $dm^6 mol^{-2} s^{-1}$. More reliably, from two sets of results we obtain a value of 13 ± 1 $dm^3 mol^{-1} s^{-1}$ for the product k_2K_a. The non-linearity of the acid plot means that the 'acidity' in this solvent is not accurately represented by the stoicheiometric concentration [H_2SO_4].

A complication in the reaction of TFA is that there are two possible enol isomers A and B and also two possible enolates C and D as outlined in Scheme 3. In hexane solution both A and B have been detected,[12] isomer A predominating with an equilibrium constant of 2.5. Another n.m.r. study[13] concludes that in the pure liquid and also in a mixture with methanol, isomer A is the only detectable constituent. Our ^1H n.m.r. measurements in acetonitrile indicate that only one isomer is present (within the error of measurement), and comparisons with the corresponding spectra of AA and HFA suggest A is the overwhelming component. This suggests that the small amount of enolate present is derived from A, *i.e.* isomer C, although we cannot exclude small contributions from B and D also. A low concentration of B might be enough to account for reaction since it is likely to be much more reactive than A. The kinetic results are not conclusive on this point. The k_1 value for TFA is *ca.* 40 times smaller than that for AA. This may reflect the deactivating effect of the CF_3 group, but equally it may result from the very small concentration of isomer B. As far as the enolate is concerned, it seems that C is the more likely reacting species given the acid-strengthening property of the CF_3 group. The corresponding k_2K_a values are 13 and 36 $dm^3 mol^{-1} s^{-1}$ for TFA and HFA. Given the expected differences in the K_a values, these figures show that as expected the enolate from TFA is the more reactive.

Table 5. Rate constants for the reaction of TBN (5×10^{-4} mol dm^{-3}) with HFA in acetonitrile.

(*a*) [H_2SO_4] = 1.09×10^{-2} mol dm^{-3}		(*b*) [HFA] = 5.81×10^{-3} mol dm^{-3}	
10^2 [HFA]/ mol dm^{-3}	k_0/s^{-1}	10^2 [H_2SO_4]/ mol dm^{-3}	k_0/s^{-1}
0.50	0.163 ± 0.012	1.15	0.198 ± 0.009
0.76	0.331 ± 0.018	2.29	0.192 ± 0.008
1.27	0.401 ± 0.019	3.44	0.172 ± 0.014
1.67	0.606 ± 0.034	4.58	0.182 ± 0.017
2.01	0.751 ± 0.019	5.73	0.202 ± 0.008

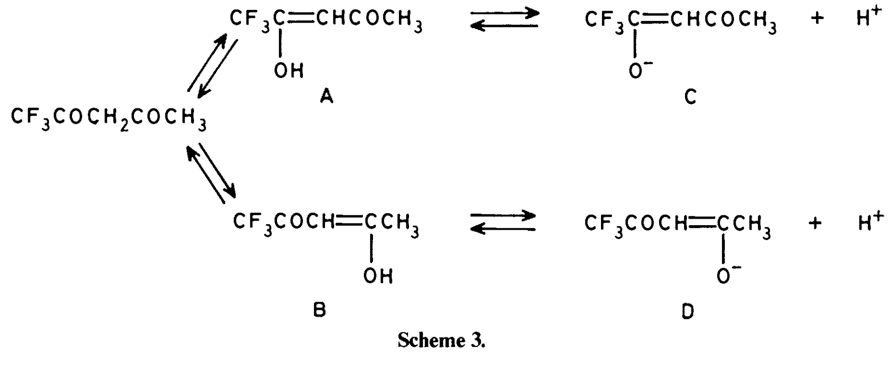
Table 6. Rate-constants for the reaction of TBN with TFA in acetonitrile.

(*a*) [H_2SO_4] = 2.34×10^{-2} mol dm^{-3}		(*b*) [HFA] = 1.45×10^{-2} mol dm^{-3}	
10^2 [TFA]/ mol dm^{-3}	k_0/s^{-1}	10^2 [H_2SO_4]/ mol dm^{-3}	k_0/s^{-1}
0.72	0.228 ± 0.009	2.34	0.445 ± 0.05
1.45	0.445 ± 0.049	4.67	0.751 ± 0.05
2.17	0.707 ± 0.040	7.01	1.22 ± 0.03
2.89	0.976 ± 0.041	9.35	1.27 ± 0.06
3.67	1.20 ± 0.02	11.7	1.65 ± 0.08

The analysis is, however, a little more complicated than so far outlined. In the absence of any added t-butyl alcohol, the measured k_0 during any one kinetic run should in fact decrease as [t-butyl alcohol] builds up from the rapid pre-equilibrium. This is not borne out experimentally, where strict first-order behaviour is noted throughout. If the pre-equilibrium [equation

$$\text{RONO} + \text{H}^+ \rightleftharpoons \text{ROH} + \text{NO}^+ \qquad (1)$$

(1)] were essentially quantitatively displaced to the right, then this would explain the kinetic order. However, this would lead to the wrong acidity dependence. An alternative explanation which does not suffer from other drawbacks, emerges if we allow for the possible rapid equilibrium hydrolysis of TBN by traces of water present in the solvent and deriving from the addition of sulphuric acid. This in fact can be demonstrated experimentally, since on mixing TBN in acetonitrile with a small quantity of sulphuric acid, an equilibrium concentration of nitrous acid is quickly formed and easily detected by the u.v. spectral changes. The nitrosating species NO^+ can then be formed from nitrous acid. This sequence is outlined in Scheme 4



Scheme 3.

Table 7. Rate constants for the reaction of IPN (2×10^{-3} mol dm^{-3}) with AA (8.08×10^{-2} mol dm^{-3}) in acetonitrile containing sulphuric acid (4.5×10^{-3} mol dm^{-3}).

(*a*) No added isopropyl alcohol		(*b*) Added isopropyl alcohol (0.02 mol dm^{-3})	
Time/s	k_0/s^{-1}	Time/s	$10^2\ k_0$/s^{-1}
0.5	0.86	5	4.1
1.0	0.79	10	3.9
1.5	0.73	15	3.9
2.0	0.69	20	3.9
2.5	0.63	25	3.6
3.0	0.59	30	3.7
3.5	0.57	35	3.6
4.0	0.54	40	3.7

Table 8. Values of k_0 for the nitrosation of TFA with nitrous acid (3×10^{-4} mol dm^{-3}) at ionic strength 1.0 ($NaClO_4$).

[TFA]/mol dm^{-3}	[$HClO_4$]/mol dm^{-3}	$10^3\ k_0$/s^{-1}
0.005	0.50	1.47
0.010	0.50	2.85
0.015	0.50	4.60
0.020	0.50	5.80
0.025	0.50	7.50
0.020	0.10	1.67
0.020	0.20	2.85
0.020	0.30	3.65
0.020	0.40	4.66

$$\mathrm{RONO} + \mathrm{H_2O} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{ROH} + \mathrm{HNO_2}$$

$$\mathrm{HNO_2} + \mathrm{H_2SO_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO^+} \xrightarrow[k_2]{\mathrm{E}} \mathrm{Products}$$

Scheme 4.

for reaction with an enol E. This suggestion is also supported by earlier experiments in this solvent starting from nitrous acid.[3] The expression for k_0 expected from Scheme 4 is given in equation 2, which reduces to the form $k_1k_2[H_2SO_4][E]/k_{-1}[H_2O]$ if both $K[H_2O] \gg [ROH]$ and $k_{-1}[H_2O] \gg k_2[E]$, and thus explains the good first-order behaviour. Further support for this mechanism comes from the fact that when isopropyl nitrite (IPN) reacts with AA under the same conditions, reactions are not strictly first order in [RONO], but when isopropyl alcohol is added, then true first-order behaviour returns. The effect is shown quite clearly in Table 7. The instantaneous first-order rate constants decrease steadily throughout the run when no isopropyl alcohol is added, whereas when 0.02 mol dm^{-3} isopropyl alcohol is added, good first-order behaviour is found. The reason why IPN is different, in this respect from TBN is that the equilibrium constant K for alkyl nitrite hydrolysis is known,[14] at least in water, to be much smaller for the secondary nitrite than for the tertiary nitrite. This is believed to be a steric effect and so is likely also to be manifest in acetonitrile solvent. This makes the inequality $K[H_2O] \gg [ROH]$ less likely to be applicable for IPN, but the change will allow for a constant k_0 when there is a large excess [ROH] present.

$$k_0 = \frac{k_1k_2[H_2SO_4][E]K[H_2O]}{(k_{-1}[H_2O] + k_2[E])(K[H_2O] + ROH]} \qquad (2)$$

(b) *Reaction with Nitrous Acid in Water*.—We have, in a previous publication,[1] shown that AA reacts with acidic solutions of nitrous acid in water *via* the enol species only. There is no evidence whatsoever of reaction *via* the enolate ion as the plot of k_0 *vs.* $[H^+]$ is linear and passes through the origin. Now we have examined the kinetics of the reaction of TFA with nitrous acid under similar conditions. It was our wish also to extend the study to include the reactions of HFA, but this compound rapidly underwent extensive hydration, which complicates the analysis of any nitrosation reaction.

Rate constants were obtained in the usual way for the nitrosation of TFA (*a*) at constant [TFA] as a function of the [acid] and (*b*) at constant [acid] and as a function of [TFA]. In both cases the ionic strength was maintained at 1.0 using sodium perchlorate, and the limiting condition $[TFA]_0 \gg [HNO_2]_0$ always prevailed. In all cases good first-order behaviour was found and the results are shown in Table 8. Reaction is strictly first order in [TFA] but the plot of k_0 *vs.* $[H^+]$ is linear with a substantial positive intercept at $[H^+] = 0$, again indicative of reaction *via* both the enol and enolate forms. Again for this substrate there are two possible enols and two possible enolates. The situation in water is somewhat different from that in acetonitrile and other non-polar solvents, in that the equilibrium constant for enolisation is much smaller in water, and the bulk of the substrate exists as the β-diketo form. The literature value[15] for K_E for TFA is 0.011, but it is not possible to establish which enol is formed or whether indeed both are present. The enol and enolate most likely to undergo nitrosation are B and D, but A and C may exist in substantially higher concentrations. Analysis of the kinetic results yields values of 46 dm^6 mol^{-2} s^{-1} for k_1 (the third-order rate constant for nitrosation of the enol) and 1.1×10^5 dm^6 mol^{-2} s^{-1} for k_2 (the corresponding constant for reaction of the enolate). The former is very close to the value of 36 dm^6 mol^{-2} s^{-1} obtained for AA, which makes it certain that we are concerned with the reaction of B and not C. Initially we would have expected k_1 to be somewhat less than 36 dm^6 mol^{-2} s^{-1} because of the expected greater electron-withdrawing capacity of $COCF_3$ compared with $COCH_3$. We cannot account for the observed result, but it must be remembered that a number of assumptions are made in the analysis (*e.g.* K_E values), which may be in error. The value of k_2 for the enolate reaction is at first sight surprisingly large at 1.1×10^5 dm^6 mol^{-2} s^{-1}, in that it is *ca.* a factor of 10 greater than that commonly believed to be the upper limit for the encounter rate between ions of opposite charge (*c.f.* the benzenesulphinate ion[8] and thiocyanate ion[16] reactions). However, a similar value has been obtained for the reaction of the enolate ion derived from dimedone,[2] and similar problems of interpretation have been encountered in the analysis of kinetic data of the halogenation reactions of enolates,[17] where the bimolecular rate constants are up to *ca.* 10^2 greater than that predicted by the Smoluchowski equation for an encounter process. As yet, no satisfactory explanation has been offered. More experimental data are required. All the derived bimolecular rate constants depend crucially upon K_E and pK_a values, and the theory may be oversimplified.

Just as for the nitrosation of dimedone, and a host of other substrates, reaction of TFA is markedly catalysed by added Cl^-, Br^-, and SCN^-. The results are given in Tables 9, 10, and 11. Again as for the uncatalysed reactions plots of k_0 *vs.* $[H^+]$ in the presence of reasonably high $[Cl^-]$, $[Br^-]$, or $[SCN^-]$, are linear with substantial positive intercepts, demonstrating again the involvement of both enol and enolate forms of the reactant. The kinetic analysis yields the values given in Table 12 for k_3 (the bimolecular rate constant for ClNO, BrNO, and ONSCN attack at the enol) and for k_4 (the corresponding rate constants for enolate reaction). Using these figures we get excellent agreement between the calculated and observed values of the slopes of k_0 *vs.* $[Cl^-]$, $[Br^-]$, and $[SCN^-]$, demonstrating the internal consistency of the analysis. In all cases the enolate is more reactive than the enol, as expected, and the now familiar[18]

Table 9. Chloride-ion catalysis in the nitrosation of TFA (0.02 mol dm^{-3}) in water with nitrous acid (3×10^{-4} mol dm^{-3}) at ionic strength 1.0 ($NaClO_4$).

$[HClO_4]$/mol dm^{-3}	$[Cl^-]$/mol dm^{-3}	$10^3\ k_0/s^{-1}$
0.10	0.40	5.86
0.20	0.40	7.77
0.30	0.40	8.93
0.40	0.40	10.1
0.50	0.40	11.8
0.20	0.00	2.40
0.20	0.10	3.80
0.20	0.20	5.26
0.20	0.30	6.75
0.20	0.50	9.16

Table 10. Bromide-ion catalysis in the nitrosation of TFA (0.02 mol dm^{-3}) in water with nitrous acid (3×10^{-4} mol dm^{-3}) at ionic strength 1.0 ($NaClO_4$).

$[HClO_4]$/mol dm^{-3}	$[Br^-]$/mol dm^{-3}	$10^3\ k_0/s^{-1}$
0.093	0.20	64.2
0.185	0.20	72.1
0.277	0.20	79.0
0.370	0.20	84.3
0.462	0.20	87.0
0.277	0.00	3.65
0.277	0.05	25.9
0.277	0.10	43.9
0.277	0.15	64.9
0.277	0.20	80.4

Table 11. Thiocyanate-ion catalysis in the nitrosation of TFA (0.01 mol dm^{-3}) in water with nitrous acid (3×10^{-4} mol dm^{-3}) at ionic strength 1.0 ($NaClO_4$).

$[HClO_4]$/mol dm^{-3}	$10^3[SCN^-]$/mol dm^{-3}	$10^3\ k_0/s^{-1}$
0.10	1.05	13.8
0.20	1.05	15.5
0.30	1.05	16.6
0.40	1.05	18.8
0.50	1.05	22.1
0.20	0.00	1.40
0.20	0.42	8.00
0.20	0.84	12.9
0.20	1.26	18.4
0.20	1.68	23.0
0.20	2.10	30.1

reactivity sequence ClNO > BrNO > ONSCN is followed. The reactions of the enolates with ClNO and BrNO are encounter-controlled since the rate constants are very close to the value of 7×10^9 dm^3 mol^{-1} s^{-1} calculated for such reactions; the enolate from dimedone behaved similarly.[2]

Table 12. Bimolecular rate constants k_3 and k_4 for the reaction of XNO with the enol and enolate, respectively, from TFA.

XNO	$k_3/dm^3\ mol^{-1}\ s^{-1}$	$k_4/dm^3\ mol^{-1}\ s^{-1}$
ClNO	4.2×10^4	1.4×10^9
BrNO	2.3×10^4	9.2×10^8
ONSCN	3.1×10^3	1.2×10^8

Conclusions

All of the kinetic results show that AA undergoes nitrosation by exclusive reaction of the enol form, whereas the trifluoro derivative TFA reacts *via* both its enol and enolate forms, whilst the hexafluoro derivative HFA reacts exclusively *via* the enolate ion. The results demonstrate the deactivating effect of CF_3 groups on electrophilic addition and also the acid-strengthening property of CF_3 groups.

Acknowledgements

We thank the SERC for a research studentship to M. J. C.

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Received 29*th November* 1988; *Paper* 8/04714F