The Mechanism of Thermal Elimination. Part 14.[1] Pyrolysis of Diacetamide, 2-Acetoxypyridine, Diacetyl Sulphide, and Thioacetic Acid: Possible Involvement of Enol Forms in Gas-phase Eliminations

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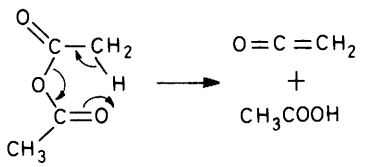
In the gas phase, diacetamide undergoes unimolecular first-order elimination to give keten and acetamide with log A 12.42 s^{-1} and E_a 158.23 kJ mol^{-1} so that the reaction proceeds *via* a cyclic six-membered transition state. At 600 K the reaction is 6.7-fold slower than the comparable pyrolysis of acetic anhydride, but 4.4-fold faster than pyrolysis of diacetyl sulphide. This shows that in contrast to ester pyrolysis, heterolysis of the C_α–X bond in these compounds is relatively unimportant, the major rate-determining step being nucleophilic attack of the carbonyl group upon the β-hydrogen; the nucleophilicity of this carbonyl group is probably enhanced by resonance with the lone pair of the group X. The very high reactivity of the diacetyl compounds relative to their ester equivalents suggests that they pyrolyse *via* the enol forms. Pyrolysis of diacetyl sulphide is accompanied by first-order decomposition of thioacetic acid (one of the primary reaction products) by a number of pathways which give rise to keten, hydrogen sulphide, carbon oxysulphide, methanethiol, and methyl thioacetate, the latter probably arising from a combination of methanethiol with unchanged thioacetic acid which also accounts for the low stoicheiometry (1.8) of the reaction. The rate of elimination of thioacetic acid is governed by the parameters log A 12.5 s^{-1} and E_a 175.7 kJ mol^{-1}; slightly different values are obtained from the acid produced by decomposition of diacetyl sulphide *viz.* 12.5 and 173.1, respectively, probably due to the differing initial proportions of the thiono- and thiolo-forms. Decomposition is much faster than the corresponding reactions of acetic acid and diacetamide, probably because the nucleophilicity of the thiol group is not lowered by resonance to the extent that operates for the corresponding nucleophiles in acetic acid and acetamide. 2-Acetoxypyridine also undergoes thermal elimination to 2-pyridone and keten, but satisfactory kinetics could not be obtained, due possibly to surface effects and an equilibrium between the *N*-acetyl and *O*-acetyl tautomers. The bulk of the compound is much more stable than diacetamide because it exists largely in the *O*-acetyl form.

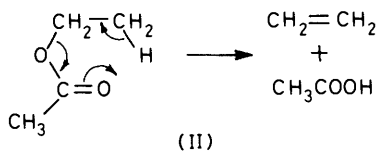
Acetic anhydride (I) was reported by Szwarc and Murawski [2] to undergo thermal elimination into keten and acetic acid with log A 12.0 s^{-1} and E_a 34.5 kcal mol^{-1}. †[Statistical analysis of their rate coefficients gives in fact log A 11.884 s^{-1} and E_a 34.01 kcal mol^{-1} (r 0.998 19).] This compound is prone to surface-catalysed decomposition and if their *minimum* rate coefficients only are used, this gives log A 12.136 s^{-1}, E_a 34.763 kcal mol^{-1} (145.49 kJ mol^{-1}) and an improved correlation coefficient of 0.999 67. We believe these latter parameters are more representative especially since theoretical calculations [3] predict log A 12.3 s^{-1}. Three points of interest emerge from these data.

(i) The elimination rate coefficient at 600 K of 296 × 10^{-3} s^{-1} is very much higher than for elimination from ethyl acetate (II) [4] for which k (600 K) = 9.81 × 10^{-6} s^{-1}. The reason for this rate difference of 30 170-fold, *i.e.* 15 085-fold per β-hydrogen, is not at all clear because polarisation of the C_α–O bond should be much easier for the acetate than for the anhydride. One contributing factor, to which we have previously drawn attention,[5] could be the activating effects of the adjacent carbonyl group upon breaking of the β-C–H bond. A β-acetyl group gives an acceleration of 388-fold per β-hydrogen,[6] whilst a β-COOMe group accelerates 144-fold per β-hydrogen, so for acetic anhydride a value in between might be expected.‡ However, this still leaves a factor of *ca.* 60-fold unaccounted for and in this paper we suggest an alternative explanation (see Discussion section).

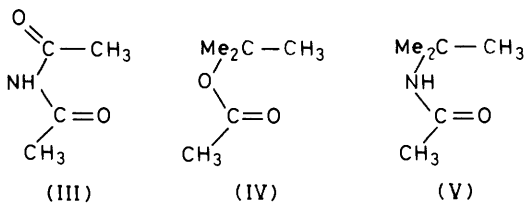
(ii) What would be the effect of replacing O by NH to give diacetamide (III)? There are many compounds which eliminate *via* a cyclic six-membered transition state and this series is aimed towards measuring as accurately as possible all the factors which determine their reactivity. Changing the C_α–O moiety to C_α–NH gives in principle a wide range of compounds, but only the effect between acetates (IV) and amides (V) has been measured, and only for the t-butyl compounds.[7,8] The respective rate coefficients at 600 K are 3.25 × 10^{-2} and 4.73 × 10^{-7} s^{-1} giving a relative rate of



(I)



(II)



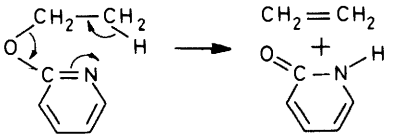
(III) (IV) (V)

† 1 cal = 4.184 J.

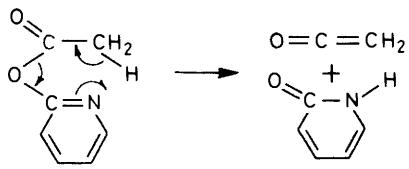
‡ Because the oxygen lone pair is conjugated with two carbonyl groups and will not be so effective in reducing the electron withdrawal by the carbonyl group.

Table 1. Kinetic data for pyrolysis of diacetamide $(MeCO)_2NH$

T/K	$10^3\ k$/s^{-1}	log A/s^{-1}	E_a/kJ mol^{-1}	Correlation coefficient r	k/s^{-1} at 600 K
546.8	1.975	12.420	158.23	0.999 58	43.7×10^{-3}
556.4	3.725				
567.1	6.70				
575.7	11.9				
580.3	15.6				
593.1	29.8				
595.1	34.8				
600.6	43.8				

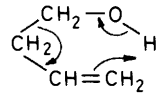


(VI)

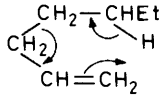


(or enol form)

(VII)



(VIII)



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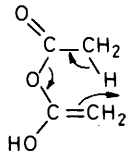
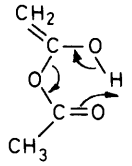
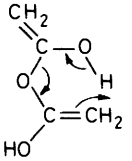


(X)



(XI)



(XII)

68 700. This very large factor derives from the fact that breaking of the C–O or C–NH bond is the principal rate-determining step in the elimination. If the same is true of the pyrolysis of acetic anhydride and diacetamide, a similarly large factor might be expected.

(iii) 3-Ethoxypyridine has been shown [9] to pyrolyse *via* a six-membered transition state (VI) to give ethene and 2-pyridone, this reaction being analogous to pyrolysis of ethyl acetate (II). Thus by analogy to pyrolysis of acetic anhydride (I) we could expect 2-acetoxypyridine to pyrolyse to keten and 2-pyridone (VII), and presumably this elimination would be much faster than that of (VI). Accordingly we have prepared 2-acetoxypyridine and determined its thermal stability.

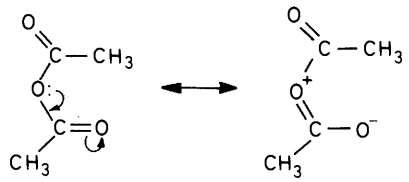
Results and Discussion

(1) *Diacetamide.*—The pyrolysis of diacetamide was very well behaved kinetically, giving very reproducible rate coefficients with no sign of any surface catalysis, *i.e.* there were no deviant runs and all rate coefficients fell precisely on the Arrhenius line. The derived log A value is that predicted for the elimination and in our experience this is the most reliable indicator of the absence or otherwise of surface catalysis; in the presence of the latter, low values are always obtained. The stoicheiometry of the reaction was 2.0 and a five-fold change in the amount of compound taken for a run gave no significant change in the rate coefficients so that the reaction is first order. Only keten and acetamide were detected as reaction products. The rate data are given in Table 1 and show that like the pyrolysis of acetic anhydride a cyclic six-membered transition state must be involved.

The rate coefficient at 600 K is 43.7×10^{-3} s^{-1} so that the elimination takes place 6.7 times more slowly than that from acetic anhydride. While this result is qualitatively in agreement with that for t-butyl acetate, *versus* *N*-t-butylacetamide, it is quantitatively very different, which suggests that breaking of the C_α–O or C_α–NH bond is *not* the most rate-determining step. Now it is generally true that for heterolytic gas-phase eliminations to occur there must be a polar bond in the transition state and breaking of this bond will be the principal rate-determining step.[10] When this is not the C_α–X bond it is usually the β-X–H bond, *e.g.* the β-O–H bond in β-hydroxy-alkenes [11] and β-hydroxy-ketones,[12] and for compounds of this type the nucleophilicity † of the group attacking the β-hydrogen obviously becomes important. For both these classes of compounds, alkyl substitution at the α-carbon produces only a small change in rate because of the lack of polarity of the C–X bond (in this case the C–CH_2 bond). The effect of polarity in the β-X–H bond is clear from the enormously greater reactivity of *e.g.* 4-hydroxybutene [(VIII); k (600 K) 1.78×10^{-4} s^{-1}] compared to hept-1-ene [13] [(IX); k (600 K) 1.34×10^{-8} s^{-1}]. With this result in mind it is possible to consider four feasible transition states for acetic anhydride pyrolysis (and likewise for diacetamide pyrolysis), *viz.* (I) and (X)—(XII).

Transition state (I) we have already shown to be difficult to reconcile with the rate data. Transition state (X) differs from it in that the attacking ' base ' is C=CH_2 instead of C=O. The relative reactivities of compounds containing one or other of these groups can vary very considerably for reasons we shall describe elsewhere. When attack is on a CH_3 group, as in ethyl acetate and ethyl vinyl ether, the reactivities are comparable,[1] so that there would be no advantage of (X) over (I), except for the presence of the HO group. Unfortunately it is not yet possible to predict the effects of substituents at this site because they vary so much in both magnitude and direction, but we note that in for example βγ-alkenoic acids,[14] a methoxy-substituent (which would be similar to hydroxy)

* It has been customary to refer to the nucleophilicity of the attacking group in papers describing pyrolytic elimination, though strictly speaking it is the basicity that should be considered.



(XIII)

increases the rate 10^5-fold at 600 K, which is very similar to the effect we are seeking to explain. On the other hand this would imply that ethyl acetate pyrolysed by the enol form and many kinetic data suggest that this cannot be so (*e.g.* the almost identical reactivities of acetates and formates [7,13,15]). Therefore we do not favour (X) but cannot entirely dismiss it. Transition state (XI) is more likely. Formation of an incipient vinyl cation will be more favourable than formation of the incipient acyl cation in (I), and the rate factor between (VIII) and (IX) is almost exactly that which we have to explain between acetic anhydride and ethyl acetates. The di(enol)ic transition state (XII) seems improbable.

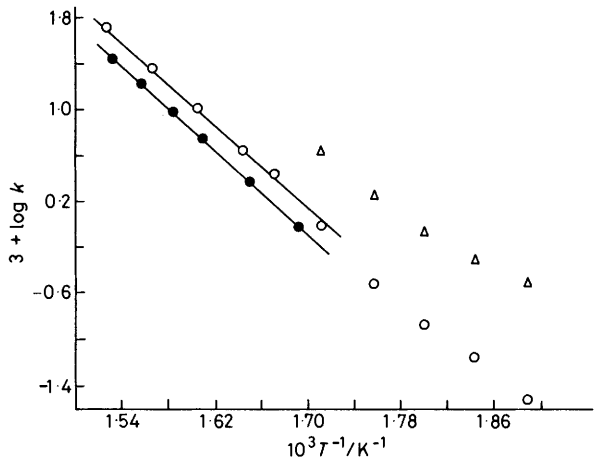
There are thus good grounds for supposing that an enolic transition state is involved. However, an additional factor needs to be taken into account. For compounds like acetic anhydride, diacetamide, *etc.* where nucleophilic attack on the β-hydrogen becomes most important, the nucleophilicity of the carbonyl group can become enhanced by resonance with the ethereal oxygen (XIII). (For acetates this can of course take place to an even greater extent, there being only one carbonyl group, but for these and related compounds, nucleophilic attack is less important.) Evidence to suggest this may be an important factor comes from pyrolysis of diacetyl sulphide, described below.

(2) *Relative Elimination Rates for Acetic Anhydride, Diacetyl Sulphide, Diacetamide, and Pentane-2,4-dione.*—Before considering these related compounds it was necessary to have an accurate rate coefficient for elimination from diacetyl sulphide at 600 K. From a kinetic study carried out between 459 and 530 K, diacetyl sulphide was reported [16] to give keten and thioacetic acid with E_a 131 kJ mol^{-1} and log A 11.02 s^{-1}. No rate coefficients were reported, and since both Arrhenius data are exceptionally low (the activation energy is about the lowest reported for any homogeneous six-centre elimination), we suspected that the reaction might be surface catalysed, even though this was said [16] not to be so. Accordingly we pyrolysed diacetyl sulphide over the temperature range 529.3—655.4 K. The reaction was accompanied by secondary decomposition of thioacetic acid though no reference to this decomposition was made in the original study; [16] decomposition is clearly evident at temperatures used in that work. Since there has not been (as far as we are aware) a previous study of the thermal decomposition of thioacetic acid, we have determined the Arrhenius data and the reactivity is discussed briefly in the next section.

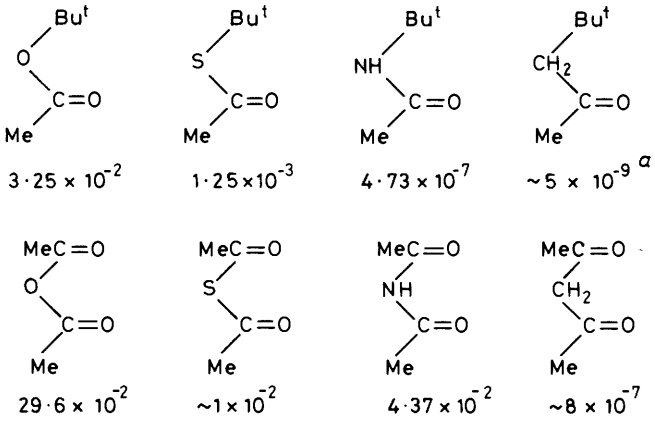
Over the temperature range 583.5—655.4 K, the initial decomposition of diacetyl sulphide is so fast that only the subsequent pyrolysis of thioacetic acid is observed. Below 583.5 K the kinetic plot could be dissected into two good first-order components. The results are plotted in the Figure, along with data obtained by pyrolysis of separately prepared thioacetic acid. The main features observable are as follows.

(i) At the highest temperatures (where surface effects are always minimal) thioacetic acid gives a good Arrhenius line, but at lower temperatures there is curvature typical of that produced by the incursion of surface catalysis.

(ii) Over the range where the Arrhenius plot for thioacetic



Arrhenius plot for pyrolysis of diacetyl sulphide and thioacetic acid: △, diacetyl sulphide; ○, thioacetic acid produced by decomposition of diacetyl sulphide; ●, authentic thioacetic acid



Scheme. Rate coefficients (k/s^{-1}) for elimination at 600 K. [a] Calculated from the published data for the ethyl compound [12] assuming that the t-butyl compound will be only 10 times as reactive because of the very low polarity of the C_α–CH_2 bond

acid is curved, so is that for diacetyl sulphide. This supports the view that over this temperature range, both compounds were subject to surface catalysis, and along with this should be noted the fact that we were never able to observe more than 25% of the decomposition of diacetyl sulphide, presumably due to an initial very fast surface-catalysed decomposition, which diminished as active sites became occupied; we were unable to improve upon this by deactivating the surface in the usual way.

(iii) Our rate coefficients for pyrolysis of diacetyl sulphide are *much* lower than those given in the literature. The rate coefficients at the two highest temperatures will be the least affected by surface effects, and these data give E_a 159 kJ mol^{-1} and log A 11.84 which seems reasonable. Since the extrapolation to 600 K from these measured rate coefficients is only a very small one the observed rate coefficient of 1×10^{-2} s^{-1} is unlikely to be in error by more than 10%; this coefficient is 42 times smaller than that given in the literature.[16]

The Scheme [2,7,8,13,17] shows the rate coefficients for elimination of t-butyl acetate and acetic anhydride and their respective analogues at 600 K. Two features are evident. First, all the compounds in the first row are less reactive than those in the

second. Secondly, the reactivity order in the second row is different from that in the first in that diacetamide is *more* reactive than diacetyl sulphide whereas one might have expected it to be less reactive. This can however be readily rationalised because whereas, in the first row, breaking of the C_α–X bond is the most important step of the reaction so that reactivity parallels the polarity of this bond, in the second row this factor is relatively unimportant, the reactivity being governed mainly by the ease of nucleophilic attack upon the β-hydrogen. The nucleophilicity of the carbonyl group will be aided by process (XIII) (and analogues) which will be more difficult for the sulphur compound than for the oxygen and nitrogen compounds. The overall reactivity is thus a balance of the ease of both C_α–X bond breakage, and nucleophilic attack upon the β-hydrogen.

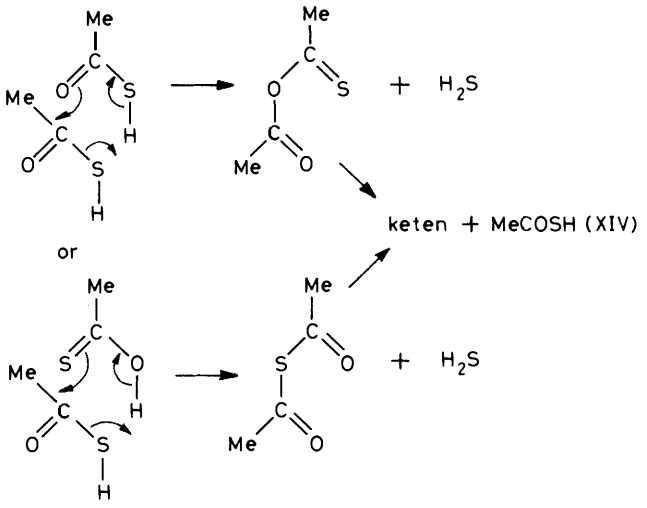
The much lower reactivity of pentane-2,4-dione relative to the O, S, and NH analogues reflects the much poorer conjugative electron release by the CH_2 group (*via* hyperconjugation) coupled with the low polarity of the C–CH_2 bond, cleavage of which is difficult as shown by the data in the first row. [The rate data for these carbon-containing compounds should not be taken too literally because the Arrhenius data [13] from which they are determined are only estimated values based on a single rate coefficient (no tests for homogeneity) and a theoretical log *A* value.]

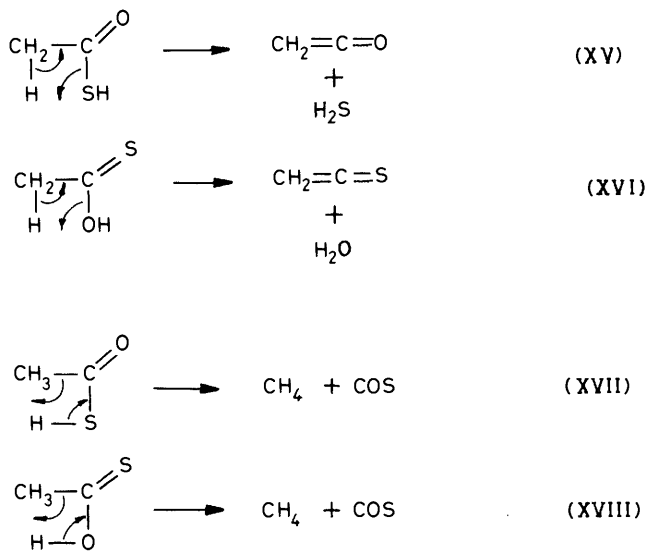
(3) *Pyrolysis of Thioacetic Acid.*—Because thioacetic acid, a by-product of the thermal decomposition of diacetyl sulphide, itself underwent elimination, and since as far as we are aware there are no kinetic data for this compound, we have made a brief study of its elimination. As this was not the main thrust of our work and because the elimination is evidently very complicated this study is incomplete; we do not plan to do further work on this compound.

The main features of the elimination are four-fold. (i) The kinetics are essentially first order. (ii) The products detected from the elimination are keten, hydrogen sulphide, carbon oxysulphide, methanethiol, and a substantial quantity of methyl thioacetate; no thioketen was detected. (iii) The stoicheiometry of the reaction was *ca.* 1.8. (iv) Thioacetic acid is much less stable than acetic acid.

Bearing in mind the known behaviour of acetic acid,[18] three possible mechanisms for decomposition of this acetic acid can be envisaged. We take into account the fact that it exists mainly in the thiolo- rather than the thiono-form. The proportion of the latter was said, on the basis of i.r. spectra obtained at 25, 70, and 100 °C, to increase with temperature.[19] However in our view the evidence was rather inconclusive because of the differing concentrations of the samples used at each temperature. Moreover, by using n.m.r. between −60 and +60 °C we were unable to detect any change in the amount of the thiono-tautomer. The product from pyrolysis of diacetyl sulphide is the thiono-form which we assume will rapidly equilibriate to the thiolo-form at high temperature. This latter we expect for reasons given below to be the more reactive, and this view is supported by the fact that the fragmentation pattern from the unchanged acid (*ca.* 80% thiolo-form) *viz*: *m/e* 76 (minor, parent ion), 61 (minor, loss of CH_3), and 43 (major, loss of SH) was different from recovered unchanged acid trapped at −78 °C, *viz.* 76 (major), 62 (large, loss of CH_2), 61 (minor), 47 (large, loss of CHO), and 43 (minor).

(i) *Second-order loss of hydrogen sulphide* (XIV). No second-order process was detected in our work and this is consistent with the lower electrophilicity of the acyl carbon in thioacetic acid compared to acetic acid. The equivalent process involving two molecules of thiono-acid would give water, keten, and dithioacetic acid (which would decompose faster).

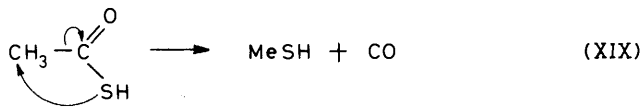




(ii) For acetic acid the equivalent of (XIV) disappears at higher temperature and is replaced by a four-centre process. For thioacetic acid this would be either (XV) or (XVI). The former is consistent with the lower stability of thioacetic acid, the C–S bond being weaker than the C–O bond, and sulphur is more nucleophilic than oxygen. Likewise acetamide undergoes the corresponding reaction more easily than does acetic acid,[20] but much less readily than does thioacetic acid. Although NH_2 should be more nucleophilic than SH, it will resonate much more strongly with the carbonyl group than will SH, so the observed result is a logical one. In contrast to (XV) process (XVI) will if anything be more difficult than for acetic acid and would give thioketen (an unknown compound) which we did not detect.

(iii) *Loss of* COS (XVII) *or* (XVIII). It is more difficult to decide whether (XVII) will be faster than for the acetic acid analogue, but it is fairly safe to assume on the basis of bond strengths that (XVII) would be faster than (XVIII). We detected carbon oxysulphide but not methane which would have escaped our analytical method.

An additional elimination is involved with thioacetic acid, namely the formation of methanethiol, presumably *via* the three-centre process (XIX) comparable with that for decarbonylation of acetyl bromide,[21] and of formamide (which



(XIX)

gives ammonia).[22] Again the high nucleophilicity of the SH group compared to OH should make this reaction faster than for acetic acid. No methanol was found so that the thionoacid does not undergo the equivalent reaction. Only a trace of methanethiol was detected in the products, but this is to be expected since it should react with thioacetic acid to give methyl thioacetate, a substantial quantity of which was obtained. This removal of thioacetic acid also accounts nicely for the stoicheiometry being less than the required 2.0.

The kinetics of the elimination were essentially first order, though below 631 K the rate coefficients during a run increased during the reaction before becoming perfectly constant. The latter portions of the kinetic runs gave reproducible rate coefficients, and the proportion of the run needed before first-order conditions were obtained increased as the temperature of the run decreased. This first-order behaviour was thus obtained immediately at 653 K but only after *ca.* 60% reaction at 591 K. There was some secondary decomposition (perhaps of keten) at 653 K but this decreased with decreasing temperature more rapidly than did the primary elimination. Rate coefficients obtained from the separately pyrolysed thioacetic acid were *ca.* 60% of those obtained from the acid produced by pyrolysis of diacetyl sulphide. In view of the different initial concentrations of the tautomers, and the competing eliminations together with removal of the thiolo-form by reaction with methanethiol, this is not altogether unexpected. From the Arrhenius data (Table 2 and Figure) the elimination rate coefficient at 600 K is *ca.* 1.6×10^{-3} s^{-1}, *i.e.* 10^8 times faster than elimination from acetic acid.[18]

(4) *2-Acetoxypyridine.*—2-Acetoxypyridine does indeed undergo the expected elimination to 2-pyridone and keten, but satisfactory kinetic data could not be obtained because the compound displayed very unusual kinetic behaviour, quite unlike that for any other compound we have studied. The abnormal features were as follows.

(i) The stoicheiometry was only *ca.* 1.6.

(ii) The kinetics were not first order, the rate coefficient decreasing with time during a given run. This discounts the possibility of polymerisation of either of the reaction products since this would give an increasing apparent rate, and moreover this is not a problem in reactions in which products are (separately) produced.

(iii) The reaction appears to be surface catalysed because in some runs an initial very fast elimination was observed. One explanation of the cessation of this fast decomposition is the gradual filling of sites on the surface, although it could arise from other reasons described below.

(iv) In runs at higher temperatures, after the initial pressure increase obtained on injecting the compound into the reactor, there followed a pressure decrease, and subsequently a slow normal pressure increase.

(v) Over the temperature range 514—728 K the approximate first-order rate coefficients showed little variation and were of the order 10^{-5}—10^{-4} s^{-1}.

There are too many complications here to permit other than a tentative explanation of the results. The low stoicheiometry derives in part from both the tendency of 2-acetoxypyridine to give some 2-pyridone on fractional distillation (presumably *via* surface-catalysed elimination), and its extreme sensitivity to moisture. (A sample left in an open vessel is completely hydrolysed to 2-pyridone and acetic acid in a few days. The odour of acetic acid is very evident on opening a vessel which has been sealed for a few days, due, presumably, to hydrolysis by water vapour in the flask, though it could be due to thermally produced keten which subsequently hydrolyses.) Thus the presence initially of some 2-pyridone in the kinetic samples could make a small contribution to the low stoicheiometry.

Another possibility is that there is an initial and very rapid elimination which is too fast to be observed. (Part of a rapid elimination was observed with some runs.) This could be due either to an initial surface catalysis, or to the fact that both *N*-acetyl and *O*-acetyl tautomers are present. If one of these eliminates much more rapidly (or slowly) than the tautomer giving rise to the bulk of the observable elimination, then the low stoicheiometry could follow, providing that both tautomers are not readily interconvertible at the elimination temperature. N.m.r. studies showed that *ca.* 10% of the *N*-acetyl derivative is present but within experimental error this was almost invariant between −35 and +50 °C so no information concerning the relative stabilities at different temperatures could be reliable deduced from this.

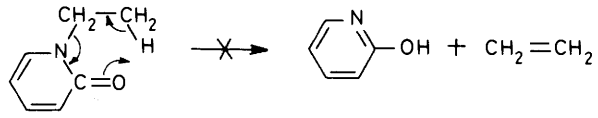
In the case of 2-ethoxypyridine pyrolysis, no elimination takes place *via* the *N*-alkyl tautomer (XX),[4,23] because the C–N bond, the breaking of which is of primary importance here, is insufficiently polar (*cf.* the low reactivity of amides compared to esters); elimination therefore takes place *via* the *O*-alkyl tautomer (VI). Nucleophilic attack on the β-hydrogen is relatively unimportant for these compounds so the advantage which (XX) would have over (VI) in this respect does not apply. For 2-acetoxypyridine however the situation is quite different. For compounds of this type nucleophilic attack on the β-hydrogen is the most important step of the reaction, and polarity of the α-C–X bond relatively unimportant (as shown by the closely similar reactivities of acetic anhydride and diacetamide). Thus the *N*-acetyl derivative (XXI) should pyrolyse faster than the *O*-acetyl tautomer (VII) and at a comparable rate to that of diacetamide (approximately half in fact due to statistical effects).

In product runs the proportion of the *N*-acetyl isomer in recovered unchanged ester appeared to diminish relative to the *O*-acetyl isomer, also suggesting that it is more reactive. This

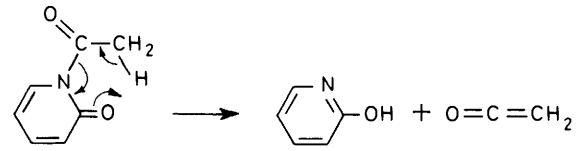
Table 2. Kinetic data for pyrolysis of diacetyl sulphide and thioacetic acid

T/K	10^3 k/s^{-1} [$(MeCO)_2S$]	10^3 k/s^{-1} (MeCOSH)
655.4		51.2
652.8		26.6 [a]
642.1		16.8 [a]
639.1		22.5
631.4		9.55 [a]
623.5		10.2
621.2		5.29 [a]
608.5		4.32
606.0		2.22 [a]
598.1		2.64
590.9		0.94 [a]
583.7	4.13	0.99
569.4	1.8	0.30
555.7	0.88	0.13
542.2	0.51	0.069
529.3	0.315	0.03

[a] Obtained from separately prepared thioacetic acid; the other data in this column are for thioacetic acid obtained by decomposition of diacetyl sulphide. The former set give E_a 175.7 kJ mol^{-1}, log A/s^{-1} 12.50, r 0.999 68, and the corresponding values for the latter are 173.1, 12.51, and 0.999 57.



(XX)



(or enol tautomer)

(XXI)

could explain the curious kinetic behaviour. The initial fast elimination could be due to pyrolysis of the *N*-acetyl tautomer and this is followed by slow pyrolysis of the *O*-acetyl tautomer or the *N*-acetyl tautomer produced by slow interconversion from the *O*-tautomer. If the *N*-tautomer, which is thermodynamically less stable, is more difficult to form at higher temperatures, then this could account for the relatively small increase in apparent reaction rate with increasing temperature. It is also possible to account for the pressure decrease noted in some runs shortly after injection of the ester into the reactor. The *N*-acetyl tautomer will pyrolyse to keten and the hydroxy-form of 2-pyridine, and these may recombine to give the *O*-acetyl tautomers which then slowly pyrolyses to the keto-form of 2-pyridone and keten. This explanation requires that the keto and enol forms of 2-pyridone are not rapidly interconvertible at high temperatures, and also makes it difficult to account for the relative insensitivity of reaction rate to temperature.

Further speculation on the cause of these anomalies is not appropriate at this time, but one can conclude that whereas 2-ethoxypyridine and ethyl acetate have similar reactivities because nucleophilic attack on the β-hydrogen is not kinetically very important, in the case of acetic anhydride and 2-acetoxypyridine, nucleophilic attack is important so that the *O*-acetyl tautomer of the latter is very much less reactive than is acetic anhydride.

Experimental

Diacetamide.—This was a commercial sample, recrystallised before use.

Diacetyl Sulphide.—This was prepared according to the literature method.[24] Acetyl chloride (54.7 g) was added to thioacetic acid (25.6 g) and the mixture heated under reflux during 5 h. Fractional distillation of the product at *ca.* 175 mmHg gave a fraction, b.p. 100—106 °C, and a main fraction, b.p. 106—111 °C. This latter was slightly pink and had n_D^{20} 1.4597, much lower than the literature value of 1.4810, and we concluded that acetyl chloride must have codistilled with the required product, despite the column having *ca.* 7 theoretical plates. The main fraction was redistilled at low pressure and a pure fraction collected, b.p. 38 °C at 5 mmHg, n_D^{20} 1.4798.

Thioacetic Acid.—A commercial sample was purified by fractional distillation, the product, b.p. 90 °C, being used for kinetic studies. It should be noted, because of the ease with which this compound undergoes elimination, the ampoules in which it is supplied can be under substantial pressure and may explode on scoring the glass if not thoroughly cooled beforehand; the temporary social results can be distressing, τ ($CDCl_3$) 4.26 (s, SH), 7.62 (s, CH_3CO), and 7.96 (s, CH_3CS); the peak height ratios of these latter two peaks measured at various temperatures between −60 and +60 °C indicated the presence of 19 ± 1% of the thiono-form.

2-*Acetoxypyridine.*—Sodium 2-pyridone was prepared by mixing stoicheiometric quantities of sodium hydroxide and 2-pyridone in water. The water was largely removed using a rotary evaporator (with a final vacuum of 0.01 mmHg) during several days. This gave a product which could be ground into a fine powder which was then dried further under high vacuum during several days.

Acetyl chloride (8.1 g, 0.103 mol) was added to sodium 2-pyridone (12 g, 0.103 mol) in dry diethyl ether at a rate sufficient to maintain reflux. The suspension of sodium chloride was removed, and the filtrate fractionally distilled to give 2-acetoxypyridine (38%, 5.4 g), τ ($CDCl_3$) 1.56 (1 H, m, *J* 5 and 2 Hz, 6-ArH), 2.19 (1 H, m, *J* 8 and 2 Hz, 4-ArH), 2.71 (1 H, m, *J* 5 and 2 Hz, 5-ArH), 2.90 (1 H, d, *J* 8 Hz, 3-ArH), 7.20 (0.3 H, s, $NCOCH_3$), and 7.69 (2.7 H, s, $OCOCH_3$). N.m.r. studies carried out between −35 and +50 °C suggested that the amount of the *N*-acetyl tautomer decreased with increasing temperature. Because of the tendency of the peak due to this compound to merge with the side bands of the *O*-acetyl peak as the temperature was lowered, studies outside the temperature range given were not possible.

Product Studies.—A solution of diacetamide in chlorobenzene was carried in a nitrogen stream down a column of heated helices at 650 K such that the residence time was *ca.* 20 s. The products were passed through a glass coil surrounded by dry ice and the effluent passed into sodium hydroxide. The contents of the cold trap were analysed by both g.l.c. and n.m.r. which indicated the presence only of dichlorobenzene and acetamide. The contents of the aqueous trap were acidified with hydrochloric acid, extracted with deuteriochloroform, and analysed by g.l.c. and n.m.r. The only product was acetic acid, produced by hydrolysis of keten.

The products from pyrolysis of thioacetic acid (under kinetic conditions) were condensed in a trap at −78 °C (and also in one experiment at −196 °C). The products were analysed by g.c.–m.s. (Kratos MS 25). The gaseous products could not be resolved from argon which is the carrier balancing gas in our kinetic system, but by monitoring for single ions in the total ion current in this region we were able to infer the presence of H_2O, CH_2CO, and COS from the *m/e* values of 34, 42, and 60, respectively; this latter was not due to acetic acid which is a trace impurity in thioacetic acid and appeared at a different point in the chromatograph. Analysis in the same way of the liquid products showed the presence of MeSH, MeCOSH (different from the starting material, see Discussion section), and MeCOSMe, the *m/e* values being 48, 76, and 90, respectively.

Product studies of 2-acetoxypyridine pyrolysis were carried out in a similar manner to that for diacetamide except that no chlorobenzene was needed and temperatures up to 740 K were used. Keten was detected by mass spectrometry of the gaseous products and 2-pyridone was obtained along with unreacted ester and was identified by its n.m.r., τ ($CDCl_3$) −3.52 (1 H, s, NH), 2.51 (1 H, t, *J* 10 Hz, 4-ArH), 2.54 (1 H, d, *J* 6.5 Hz, 6-ArH), 3.39 (1 H, d, *J* 10 Hz, 3-ArH), and 3.69 (1 H, t, *J* 6.5 Hz, 5-ArH). The peak in the n.m.r. of the unchanged ester, due to the *N*-acetyl group, tended to be smaller in the recovered material, indicating that this tautomer is more reactive than the *O*-acetyl form.

Kinetic Studies.—These were carried out in the manner and apparatus previously described.[25] Diacetamide was injected into the reactor as a solution in chlorobenzene. The kinetic data are given in Tables 1 and 2 and displayed in the Figure. The Arrhenius parameters for decomposition of thioacetic acid produced from diacetyl sulphide are calculated only from those points which are evidently on a linear plot and therefore free from surface catalytic effects.

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