Reactions of Keten. Part IV.† Kinetics and Thermodynamics of the Gas-phase Reaction: Thioacetic Acid + Keten $\rightleftharpoons$ Acetic Thioanhydride

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The homogeneous gas-phase reaction $CH_3COSH + CH_2{:}CO \rightleftharpoons Ac_2S$ has been studied in both directions over the temperature range 128—253°. The forward reaction is of the second order, $k = 10^{5\cdot46} \exp(-37{,}900/RT)$ l mol^{-1} s^{-1}, and the back reaction first order, $k = 10^{11\cdot02} \exp(-131{,}000/RT)$ s^{-1}. Equilibrium constants were measured starting from both sides of the reaction, and calculated from the ratio of the rate constants. From the mean of these was obtained $\Delta H^\circ = -94\cdot7$ kJ mol^{-1} and $\Delta S^\circ = -140\cdot8$ J K^{-1} mol^{-1}. Results are compared with those obtained for the keten–acetic acid system.

THE gas-phase addition of acetic acid to keten is a homogeneous second-order reaction,[1] the back reaction of which is the unimolecular decomposition of acetic anhydride.[2] The reactions are amenable to analysis and the kinetic and thermodynamic parameters known. It is of interest to compare the system with one in which oxygen is replaced by sulphur. Complete substitution is not feasible for reasons of instability, and in the work reported here only one oxygen, in acetic acid, is replaced. In this case the existence of thiolo- and thiono-isomers of the acid introduces a possible complication.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus was of a conventional static type with a glass spiral manometer and heated dead spaces. Unpacked and packed silica vessels had surface : volume ratios of 0·89 and 9·80 cm^{-1} respectively, and were in some cases carbon coated before use by pyrolysing acetic acid in them at 600°. Temperatures were controlled to better than $\pm 0\cdot2^\circ$ electronically and measured by calibrated chromel–alumel thermocouples.

Kinetic and equilibrium runs in the forward direction were carried out by adding thioacetic acid and keten separately to the vessel. It was not possible to premix the reactants since reaction rates were appreciable at temperatures needed to prevent condensation. Runs in which either keten or acid was admitted to the vessel first gave the same rate constants. Rates of reaction and equilibrium constants in both directions were measured by the amount of keten forming or disappearing and by pressure change. At the end of each run the vessel contents, which comprised keten, thioacetic acid, and acetic thioanhydride only, were passed into a trap at −90°. Keten did not condense and was measured in a gas burette and by i.r. absorption at 2150 cm^{-1}. Thioacetic acid and acetic thioanhydride were identified by i.r. and u.v. analysis but it was not found possible to measure one quantitatively in the presence of the other. Rate constants were calculated from initial rates or from the second-order plot appropriate to the relative concentrations of keten and thioacetic acid.[1]

Materials.—Keten was prepared by the pyrolysis of acetic acid in a flow system at 400°, followed by low-temperature fractionation. It was stored *in vacuo* at −183° and the amount needed for each run redistilled at −90° before use. Thioacetic acid ($\geqslant$98%) was fractionally distilled under vacuum and redistilled immediately before use. Acetic thioanhydride (97%) was redistilled under vacuum.

RESULTS AND DISCUSSION

Rates and equilibria for the gas-phase addition of thioacetic acid to keten have been studied in the temperature range 128—228°, and for the thermal decomposition of acetic thioanhydride in the range 186—253°. Acetic thioanhydride was the sole product detected in the former reaction and only keten and thioacetic acid were formed in the thermal decomposition. Dimerisation of keten was not significant under these conditions since keten pressures did not exceed 20 Torr (1 Torr = 133·28 N m^{-2}).

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† Part III, P. G. Blake and H. H. Davies, *J.C.S. Perkin II*, 1972, 321.

[1] P. G. Blake and H. H. Davies, *J. Chem. Soc.* (*B*), 1971, 1727.

[2] P. G. Blake and A. Speis, *J. Chem. Soc.* (*B*), 1971, 1877.

The products and the relation between pressure change and Δ(keten), which is shown in Table 1 for both forward and back reactions, indicate that the system is correctly represented by equation (1).

TABLE 1

Relation between Δp and Δ(keten) for forward and back reactions

T/°C	Δp/Torr	Δ(keten)/ Torr	Mean ratio Δp/ Δ keten
	Back reaction		
197·9	1·12	1·18	
207·7	1·67	1·74	
216·0	2·12	2·09	1·00 ± 0·03
216·0	2·30	2·22	
228·0	2·26	2·19	
228·0	2·39	2·36	
	Forward reaction		
140·0	9·02	9·01	
140·0	8·84	8·77	1·00 ± 0·01
140·0	9·17	9·24	
140·0	8·96	8·96	

$$\mathrm{CH_2{:}CO + CH_3COSH \rightleftharpoons Ac_2S} \qquad (1)$$

Kinetics.—The forward reaction is second order overall, being first order in both keten and acid (Figure 1). Actual slopes are 1·03 ± 0·04 for keten and 0·97 ± 0·04 for thioacetic acid. The Arrhenius equation is $k = 10^{5\cdot43 \pm 0\cdot25} \exp(-37{,}900 \pm 900/RT)$ l mol^{-1} s^{-1} (R = 8·314 J K^{-1} mol^{-1}). The reverse decomposition of acetic thioanhydride is of the first order, $k = 10^{11\cdot02 \pm 0\cdot67} \exp(-131{,}000 \pm 6400/RT)$ s^{-1}. Both forward and back reactions are homogeneous (carbon coating the vessels and changing the surface : volume ratio by a factor of 11 had little effect) and their rates are unaffected by the addition of isobutene as inhibitor.

TABLE 2

Comparison of calculated and experimental fractions of reaction in forward and reverse directions (Z = reactional change)

	Forward reaction		Reverse reaction	
t/s	Z (expt.)	Z (calc.)	Z (expt.)	Z (calc.)
15			0·0387	0·0380
30	0·143	0·143	0·0743	0·0732
60	0·252	0·250	0·139	0·139
90	0·331	0·312	0·196	0·197
120	0·400	0·400	0·242	0·246
180	0·500	0·496	0·320	0·321
300	0·613	0·616	0·401	0·402
600	0·744	0·748	0·446	0·446
1200	0·824	0·826	0·448	0·450
2400	0·858	0·858	0·450	0·450

Thermodynamics.—Equilibrium constants were measured starting with both thioacetic acid and keten and with acetic thioanhydride. These are plotted in Figure 2, which also shows the Van't Hoff plot calculated from the ratio of the forward and backward rate constants. These were obtained under conditions far removed from equilibrium; their applicability at equilibrium was tested by substituting them into the integrated equations for opposing reactions of the second and first order, and comparing the fraction of reaction predicted at various times with those observed experimentally. Table 2 shows the results of this comparison in both directions and that the rate constants are valid at equilibrium.

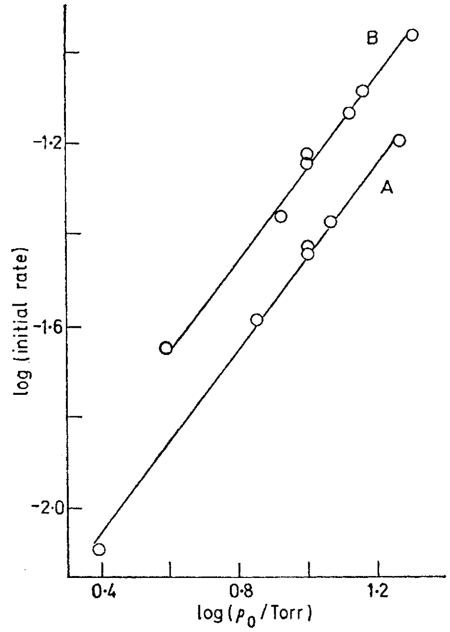


FIGURE 1 Orders in keten and thioacetic acid at 193°. Plot of log (initial rate) against A, log(keten) or B, log(thioacetic acid) initial pressure, the initial pressure of the other reactant remaining constant at 10 Torr. The keten order plot is displaced downwards by 0·2 log units for clarity

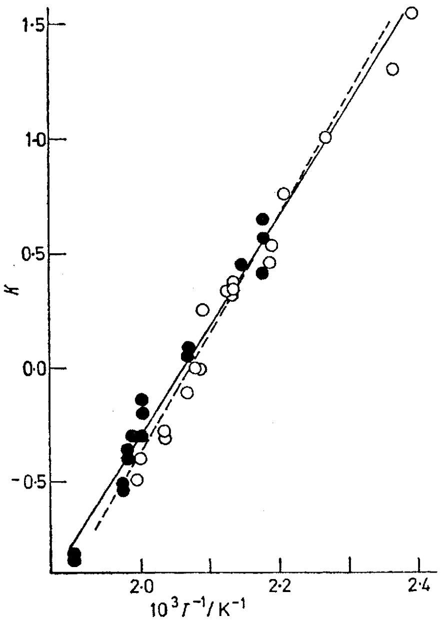
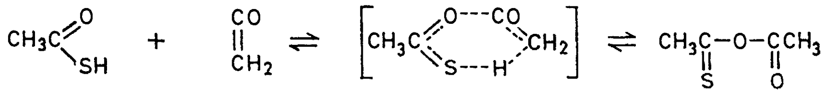


FIGURE 2 Temperature dependence of equilibrium constant $K = p[\mathrm{Ac_2S}]/p[\mathrm{CH_2{:}CO}] \times p[\mathrm{CH_3COSH}]$: ○, K from forward direction; ●, K from reverse direction; ---- line obtained from ratio of kinetic data for forward and reverse reaction

The thermodynamic results obtained from independent least-squares treatment of the three sets of equilibrium constants are given in Table 3. The entropy change is with respect to a standard state of 1 atmosphere and the mean temperature is 450 K. Mean values are $\Delta H^\circ = -94{\cdot}7$ kJ mol^{-1} and $\Delta S^\circ = -140{\cdot}8$ J K^{-1} mol^{-1}.

Mechanism.—The kinetics and thermodynamics of the system closely resemble those of the reaction of acetic acid with keten (Table 4). This makes it likely that reaction proceeds *via* a corresponding six centre transition state. However, the presence of the sulphur atom introduces a complication in that the thiolo-acid would then give rise to acetic thioacetic anhydride [reaction (2)]. Similarly thionoacetic acid and acetic thioanhydride would be connected through another six-membered transition state [reaction (3)].


(2)

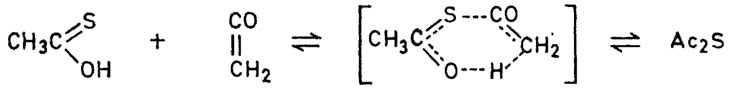

(3)

Table 3

Thermodynamic data for reaction (1)

Source of data	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
K (forward)	$-91{\cdot}44 \pm 4{\cdot}1$	$-134{\cdot}5 \pm 6{\cdot}3$
K^{-1} (reverse)	$-95{\cdot}47 \pm 9{\cdot}7$	$-141{\cdot}7 \pm 14{\cdot}4$
k (forward)/*k* (reverse)	$-97{\cdot}22 \pm 6{\cdot}6$	$-146{\cdot}3 \pm 14{\cdot}3$

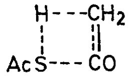
Table 4

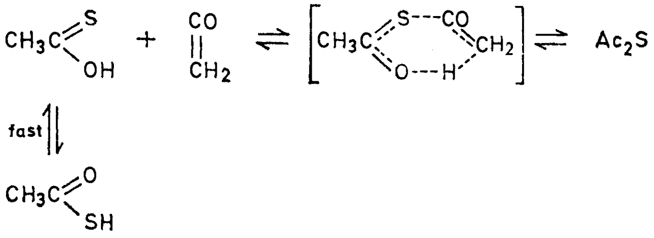
Comparison of kinetic and thermodynamic results for the reactions of thioacetic acid and acetic acid with keten

Parameter	$CH_3COSH + CH_2{:}CO \rightleftharpoons Ac_2S$	$CH_3CO_2H + CH_2{:}CO \rightleftharpoons Ac_2O$
E_c (forward)/kJ mol^{-1}	37·9	46·3
A (forward)/l mol^{-1} s^{-1}	$10^{5{\cdot}43}$	$10^{5{\cdot}81}$
E (backward)/kJ mol^{-1}	131·0	134·7
A (backward)/s^{-1}	$10^{11{\cdot}02}$	$10^{11{\cdot}27}$
ΔH°/kJ mol^{-1}	$-94{\cdot}7$	$-87{\cdot}5$
ΔS°/J K^{-1} mol^{-1}	$-140{\cdot}8$	$-128{\cdot}7$

Thioacetic acid consists mainly of the thiolo-form at room temperature but the proportion of thiono-acid increases with increasing temperature.[3] In addition there is rapid interchange between the forms even under non-polar conditions.[4] No evidence was obtained in this work for the existence of acetic thioacetic anhydride. The thioacetic acid obtained from the decomposition of acetic thioanhydride was always identical with the reagent used in the forward reaction, which is not surprising in view of the rapid exchange between the two acid forms and the sampling method of analysis used.

A four-centre transition state (A) may be postulated to avoid this complication but the low *A* factor of $10^{11{\cdot}0}$ s^{-1} for the back reaction and the general similarity to the acetic anhydride system make this improbable. The mechanism in the Scheme is therefore proposed. Keten reacts preferentially with the thiono-acid; in the decomposition of acetic thioanhydride, thionoacetic acid is formed first and rapidly equilibrates, leading to mainly thioloacetic acid at room temperature. The reaction of thiono-acid with keten may be regarded as proceeding by nucleophilic attack of sulphur on the carbonyl carbon of keten,[5] which carries a net positive charge of 0·49 e.[6]


(A)



Scheme

This reaction is much faster than when the weaker nucleophile oxygen is the attacking agent, as would be the case with thioloacetic acid.

The rate of addition of thioacetic acid to keten is some four times faster than that of acetic acid. This is due to the lower activation energy, which outweighs the slightly unfavourable *A* factor in the thio-acid case. However the true rate constant for the reaction of thionoacetic acid with keten must be greater than the rate constant reported for total thioacetic acid and cannot be determined since the proportion of thiono-form is unknown. It is reasonable to expect the rate of addition of thioloacetic acid to keten to be less than that of acetic acid, since it is a stronger acid [7] and Briody *et al.*[5] have shown that the rate of addition of weak acids to dimethylketen is inversely proportional to their strength.

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[5] J. M. Briody, P. J. Lillford, and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 885.

[6] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1970, 1016.

[7] J. Hipkin and D. P. N. Satchell, *Tetrahedron*, 1965, **21**, 835.