317.   *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part XIII.[1] The Initial Rates of the Oxidations of Formic and Malonic Acids.*

By T. J. KEMP and WILLIAM A. WATERS.

The oxidation of formic acid is of first order with respect to [V] and, by replacement of formic acid by [C-^{2}H]formic acid, the kinetic isotope effect, k_H/k_D has been found to be 4·1 at 61·5°. The oxidation of malonic acid requires the inclusion of a $[V^V]^2$ term in the kinetic equation.

In Part I[2] it was reported that formic and malonic acids are not easily oxidised by vanadium(v), which is in contrast to the ease of oxidation of malonic acid by manganic pyrophosphate.[3] However, by carrying out the reactions at a higher temperature and by using greater reactant concentrations than have been hitherto necessary, we have determined the kinetic features of the initial stages of the slow oxidations of formic, [C-^{2}H] formic, and malonic acids by vanadium(v) sulphate. In Parts II[4] and III[5] of this series it was shown that this oxidant is a mixture containing (hydrogen sulphate) complexes, and we have therefore compared reaction velocities only in solutions of constant hydrogen sulphate concentration, by use of sulphuric acid in the concentration range corresponding to its dissociation as a strong monobasic acid. The vanadium(v) solutions were prepared (cf. Part II)[4] from ammonium metavanadate, and complete reaction according to the equation

$$2H_2SO_4 + NH_4VO_3 \longrightarrow VO_2^+ + NH_4^+ + H_2O + 2HSO_4^-$$

was presumed to occur. When [V^V] was varied, adjustment of [HSO$_4^-$] was made by addition of sodium hydrogen sulphate.

RESULTS

The Oxidation of Formic Acid.—The reaction was of the first order with respect to both oxidant and substrate concentrations [Table 1, (*a*) and (*b*)]. Variation of the concentration of acid did not greatly affect the reaction rate; Table 1(*c*) shows that a ten-fold increase in [H$_2$SO$_4$] may increase the rate by 20—50%. The effect of deuterium substitution at the C–H bond of the formic acid was to reduce the reaction rate by a factor of four at 61·5° [Table 1(*d*)]. The rate was unaffected when manganous ions were introduced into the medium under conditions of constant ionic strength [Table 1(*e*)]. From the temperature-dependence of the reaction rate [Table 1(*f*)], we have been able to calculate the Arrhenius parameters for the oxidation.

The Oxidation of Malonic Acid.—The initial oxidation rate showed the following dependence upon the oxidant concentration [Table 2(*a*)]:

$$-\Delta[V^V]/\Delta t \ (10^{-7} \text{ mole l.}^{-1} \text{ sec.}^{-1}) = 37[V^V] + 1960 \ [V^V]^2.$$

The reaction was of the first order with respect to the malonic acid concentration [Table 2(*b*)], but the rate was not very sensitive to variation of the acidity of the medium [Table 2(*c*)]. With regard to the introduction of other metal ions into the reaction medium: (i) the effect of vanadium(IV) ions was to leave the rate unaltered, whereas (ii) manganous ions greatly accelerated the rate [Table 2(*d*)]. A more detailed account of the latter observation will be published subsequently. The energy of activation for the oxidation

[1] Part XII, Jones and Waters, *J.*, 1963, 352.
[2] Littler and Waters, *J.*, 1959, 1299.
[3] Drummond and Waters, *J.*, 1954, 2456.
[4] Littler and Waters, *J.*, 1959, 3014.
[5] Littler and Waters, *J.*, 1959, 4046.

was found to be 19·7 kcal./mole [Table 2(*e*)]. The great ease of oxidation of α-hydroxy-acids [6] by vanadium(v) precludes attempts to isolate intermediate products but formic acid was positively identified as an eventual oxidation product. By analogy, therefore,

TABLE 1.

The oxidation of formic acid by vanadium(v) sulphate.

(*a*) Dependence of the initial rate on oxidant concentration.

Temperature = 61·3°, $[HCO_2H]$ = 0·972 moles l.$^{-1}$, $[H_2SO_4]$ = 2·276 moles l.$^{-1}$. The salt concentration was adjusted to 0·258 moles l.$^{-1}$ by means of sodium hydrogen sulphate.

$[V^V]$ (moles l.$^{-1}$)	0·0516	0·0774	0·1032	0·129
$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	2·23	3·11	4·46	5·55
$\{-\Delta[V^V]/\Delta t\}/[V^V]$ (10^{-7} sec.$^{-1}$)	43·2	40·2	43·2	43·0

(*b*) Dependence of the initial rate on substrate concentration.

Temperature = 57·9°, $[V^V]$ = 0·0725 moles l.$^{-1}$, $[H_2SO_4]$ = 1·655 moles l.$^{-1}$, $[HSO_4^-]$ = 0·145 moles l.$^{-1}$.

$[HCO_2H]$ (moles l.$^{-1}$)	1·32	2·11	3·165	4·22	5·275
$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	2·79	4·67	7·00	10·15	12·9
$\{-\Delta[V^V]/\Delta t\}/[HCO_2H]$ (10^{-7} sec.$^{-1}$)	2·11	2·21	2·21	2·41	2·45

(*c*) Dependence of the initial rate on acidity.

Temperature = 57·9°, $[V^V]$ = 0·0725 moles l.$^{-1}$, $[HCO_2H]$ = 6·625 moles l.$^{-1}$, $\{[H_2SO_4] + [HSO_4^-]\}$ = 2·58 moles l.$^{-1}$ (control by addition of NaHSO$_4$).

$[H_2SO_4]$ (moles l.$^{-1}$)	$[NaHSO_4]$ (moles l.$^{-1}$)	$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	$[H_2SO_4]$ (moles l.$^{-1}$)	$[NaHSO_4]$ (moles l.$^{-1}$)	$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)
0·155	2·425	18·1	1·523	1·057	22·0
0·725	1·857	18·9	1·98	0·60	24·3
1·067	1·513	21·3	2·435	0·145	25·7

(*d*) Primary kinetic isotope effect for the oxidation.

Temperature = 61·5°, $[V^V]$ = 0·0725 moles l.$^{-1}$, $[H_2SO_4]$ = 1·655 moles l.$^{-1}$.

[Acid] (moles l.$^{-1}$)	$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	$\{-\Delta[V^V]/\Delta t\}/[\text{Acid}]$ (sec.$^{-1}$)	k_H/k_D
HCO$_2$H 0·437	1·39	3·18⎫	
DCO$_2$H 0·228	0·178	0·78⎭	4·1

(*e*) Test for a specific manganous ion effect on the initial rate.

Temperature = 61·3°, $[HCO_2H]$ = 1·94 moles l.$^{-1}$, $[H_2SO_4]$ = 2·206 moles l.$^{-1}$, $[V^V]$ = 0·0967 moles l.$^{-1}$.

$[Mn^{II}]$ (moles l.$^{-1}$)	$[Zn^{II}]$ (moles l.$^{-1}$)	$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)
0	0·1155	8·15
0·1155	0	7·61

(*f*) Temperature-dependence of the initial rate.

$[HCO_2H]$ = 6·625 moles l.$^{-1}$, $[V^V]$ = 0·2175 moles l.$^{-1}$, $[H_2SO_4]$ = 0·465 moles l.$^{-1}$.

Temperature	33·0°	41·4°	49·6°	58·1°
$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	3·91	10·12	25·9	66·5

Hence, $\Delta E^\ddagger$ = 22·8 kcal./mole, $\Delta H^\ddagger$ = 22·2 kcal./mole, $\Delta S^\ddagger$ = −17 e.u., $\Delta F_{298°}^\ddagger$ = 27·3 kcal./mole, k_2 (calc.)$_{298°}$ = 0·97 × 10^{-7} l.mole^{-1} sec.$^{-1}$.

we assume that the course of oxidation resembles that for oxidation by manganic pyrophosphate, *i.e.*,

$$CH_2(CO_2H)_2 \longrightarrow HO \cdot CH(CO_2H)_2 \longrightarrow OCH \cdot CO_2H \longrightarrow HCO_2H$$
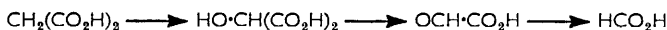
DISCUSSION

The hypothesis that the one-electron oxidation of aldehydes occurs by way of enolisation was tested for vanadium(v) in Part XII.[1] The much less facile oxidation by vanadium(v) of formaldehyde,[7] a molecule which cannot enolise, occurs through the hydrate,

[6] Jones, Waters, and Littler, *J.*, 1961, 630.
[7] Kemp and Waters, *Proc. Roy. Soc.*, 1963, *A*, **274**, 480.

TABLE 2.

The oxidation of malonic acid by vanadium(v) sulphate.

(a) Dependence of the initial rate on oxidant concentration.

Temperature = 56·5°, $[CH_2(CO_2H)_2]$ = 0·338 moles l.$^{-1}$, $[H_2SO_4]$ = 1·81 moles l.$^{-1}$. The salt concentration was adjusted to 0·29 moles l.$^{-1}$ by means of sodium hydrogen sulphate. The observed initial rates are compared with those derived from the expression:

$$-\Delta[V^V]/\Delta t \ (10^{-7} \text{ mole l.}^{-1} \text{ sec.}^{-1}) = 37[V^V] + 1960[V^V]^2$$

$[V^V]$ (moles l.$^{-1}$)	0·0290	0·0508	0·0725	0·0943	0·109	0·1305	0·145
$37[V^V]$	1·075	1·88	2·68	3·5	4·0	4·8	5·4
$1960[V^V]^2$	1·645	5·05	10·3	17·5	23·3	33·3	41·1
Calc. rate } $-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	2·72	6·93	13·0	21·0	27·3	38·1	46·5
Obs. rate }	3·00	6·89	12·1	21·3	26·4	39·7	46·8

(b) Dependence of the initial rate on substrate concentration.

Temperature = 55·6°, $[V^V]$ = 0·145 moles l.$^{-1}$, $[H_2SO_4]$ = 0·310 moles l.$^{-1}$.

$[CH_2(CO_2H)_2]$ (moles l.$^{-1}$)	0·169	0·338	0·507	0·677
$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	11·5	20·2	30·1	41·4
$\{-\Delta[V^V]/\Delta t\}/[CH_2(CO_2H)_2]$ (10^{-7} sec.$^{-1}$)	68	60	60	61

(c) Dependence of the initial rate on the molar concentration of sulphuric acid.

Temperature = 55·4°, $[V^V]$ = 0·0725 moles l.$^{-1}$, $[CH_2(CO_2H)_2]$ = 0·338 moles l.$^{-1}$, $\{[H_2SO_4] + [HSO_4^-]\}$ = 2·58 moles l.$^{-1}$ (H_2SO_4 was replaced by an equivalent amount of $NaHSO_4$).

$[H_2SO_4]$ (moles l.$^{-1}$)	0·155	0·611	0·953	1·295	1·865	2·435
$-\Delta[V^V]/dt$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	9·64, 9·65	9·88	11·0	11·6	13·3	16·3, 16·9

(d) Effects on the initial rate of oxidation, of introducing vanadium(iv) and manganous ions into the reaction medium.

In the presence of vanadium(iv), the rate was followed by observing the decrease in the vanadium(v) absorption, in a 2 mm. cell, at 375 mμ (ϵ 42·2) at which wavelength vanadium(iv) absorbs feebly.

(i) Effect of vanadium(iv) ions.

$[V^V]$ = 0·1086 moles l.$^{-1}$, $\{[ZnSO_4] + [VOSO_4]\}$ = 0·075 moles l.$^{-1}$, $[CH_2(CO_2H)_2]$ = 0·338 moles l.$^{-1}$, $[H_2SO_4]$ = 1·74 moles l.$^{-1}$.

Temp.	$[VO^{2+}]$ (moles l.$^{-1}$)	$[Zn^{2+}]$ (moles l.$^{-1}$)	$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)
59·8°	0·075	0	17·7
59·8	0	0·075	18·8
61·6	0·075	0	21·0
61·6	0	0·075	22·7

(ii) Effect of manganous ions.

Temperature = 47·1°, $[CH_2(CO_2H)_2]$ = 0·338 moles l.$^{-1}$, $[H_2SO_4]$ = 1·655 moles l.$^{-1}$, $\{[ZnSO_4] + [MnSO_4]\}$ = 0·260 moles l.$^{-1}$, $[V^V]$ = 0·0725 moles l.$^{-1}$.

$[Mn^{2+}]$ (moles l.$^{-1}$)	$[Zn^{2+}]$ (moles l.$^{-1}$)	$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)
0	0·260	5·03
0·0260	0·234	42·5

(e) Temperature-dependence of the initial rate.

$[V^V]$ = 0·1015 moles l.$^{-1}$, $[H_2SO_4]$ = 1·717 moles l.$^{-1}$, $[CH_2(CO_2H)_2]$ = 0·520 moles l.$^{-1}$, $[ZnSO_4]$ = 0·156 moles l.$^{-1}$.

Temperature	25·4°	27·1°	30·8°	36·7°	42·8°	50·2°	55·6°	60·55°
$-\Delta[V^V]/\Delta t$ (10^{-7} mole l.$^{-1}$ sec.$^{-1}$)	1·35	1·87	2·34	5·15	8·55	20·6	31·3	47·3

Hence, $\Delta E^{\ddagger}$ = 19·7 kcal./mole.

$CH_2(OH)_2$, and can be regarded as an oxidation of an alcohol, for the kinetic isotope effect (k_H/k_D = 4·6 at 50°) and the kinetic parameters $\Delta E^{\ddagger}$ and $\Delta S^{\ddagger}$ all closely resemble those found for cyclohexanol. With formaldehyde, however, the rate equation was shown to have the form

$$d[V^V]/dt = k[\text{Aldehyde}] \{[V^V][H_3O^+] + k' \ [V^V]^2[H_3O^+]^2\},$$

and in order to explain this, it was suggested that the oxidation occurred by the breakdown of either of two complexes, A or B.

The ion formulated as $V(OH)_2{}^{2+}$ would immediately break down to the vanadyl cation:

$$V(OH)_2{}^{2+} \longrightarrow VO^{2+} + H_2O$$

Only complex A decomposes to give a free radical, C this being the normal route for the oxidation of a monohydric alcohol;[5] the complex B, by concerted electron movements, immediately gives formic acid (R = H).

Towards many oxidants, formic acid behaves as an aldehyde, and our kinetic study of the oxidations of formic acid and [C-^{2}H]formic acid now shows that, towards vanadium(v), formic acid behaves like a monohydric alcohol, by breaking down after forming only a binary complex of type A; C–H bond fission is an essential feature of the rate-determining reaction since k_H/k_D has the value 4·1 at 61·5°, corresponding to which an activation energy difference of 0·94 kcal./mole can be calculated for the isotopic substitution. Moreover, the Arrhenius parameters for oxidation of formic acid by vanadium(v) [Table 1(f)] are not dissimilar to those found for formaldehyde.
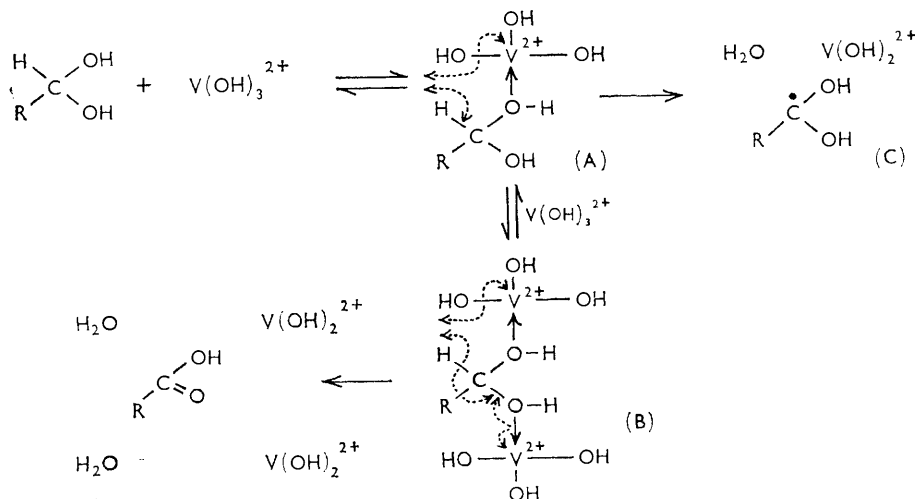
The oxidation of malonic acid by vanadium(v) is of interest because it illustrates significant differences between this oxidant and manganic pyrophosphate. Drummond and Waters[3] found that the latter oxidation involved initial complex formation, that it was specifically retarded by the addition of manganous ions, and that it produced a transient free radical of considerable oxidative power. They therefore suggested that the reversible reaction

$$\{CH_2(CO_2H)_2,Mn(H_3P_2O_7)_2\}^+ \rightleftharpoons Mn(H_3P_2O_7)_2 + {\cdot}CH(CO_2H)_2 + H^+$$

was involved in this oxidation, the free radical ·CH(CO$_2$H)$_2$ having a redox potential comparable with that of Mn^{III}/Mn^{II} pyrophosphates. Now, although vanadium(v) sulphate has a higher redox potential than manganese(III) pyrophosphate, a similar mechanism cannot be relevant for the vanadium(v) oxidation of malonic acid, for this reaction is not retarded by the introduction of either vanadium(IV) or manganous ions [Table 2(d)]; in fact, the manganous ion is a positive and not a negative catalyst.

Table 2(a) shows that the kinetic equation for the oxidation of malonic acid by vanadium(v) involves a term in [vanadium(v)]^2 which becomes dominant at vanadium(v) concentrations over 0·03 moles l.$^{-1}$. As the oxidation of formaldehyde has shown, this portion of the oxidation requires the formation of a ternary complex (*e.g.*, B) which could break down without the transient formation of an organic free radical. Thus, under the conditions described in Table 2(c), the absence of retardation by vanadium(IV) or manganous ions is not surprising.

EXPERIMENTAL

Materials. Malonic acid was recrystallised from 5% ethanol–benzene, and had m. p. 135·5. AnalaR grade formic acid was freshly distilled. Vanadium(v) sulphate solutions were made from ammonium metavanadate and standardised by the method described by Littler and Waters,[2,4] and the total salt concentration was adjusted, when necessary, by adding sodium hydrogen sulphate, taking $NH_4VO_3 \equiv 2NaHSO_4$. The preparation and standardisation of deuterated formic acid have been referred to previously.[7]

Reaction rates were determined by measuring the increase of vanadium(IV) absorption, at 750 mμ, of the reaction solution, by use of a 1 cm. cell and an Adkins thermostatically controlled cell-block placed in a Unicam S.P. 500 spectrophotometer.

The only departure from this practice was made when large amounts of vanadium(IV) were initially present, and in this case, the far less sensitive method of observing the decrease of vanadium(v) absorption was employed [Table 2(*d*)(i)].

Formic acid was isolated from a vanadium(v) sulphate (1 mol.)–malonic acid (1 mol.) reaction mixture, which had been standing at room temperature for 12 days, by use of the technique of Drummond and Waters,[3] chromotropic acid being used for the detection of formic acid.