The Kinetics and Mechanisms of Additions to Olefinic Substances. Part XII.[1] Kinetics of Addition initiated by Chlorine Acetate

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The kinetics of the reactions of electrophilic chlorine acetate with methyl *p*-nitro-*trans*-cinnamate in acetic acid and in acetic acid containing various proportions of water, and of the similar reactions of methyl *p*-chloro-*trans*-cinnamate. of *trans*-1-nitro-2-phenylethylene, and of acrylic acid in aqueous acetic acid are described. The results confirm that the principal reagent effective under these conditions is molecular chlorine acetate. Catalysis by added mineral acid, indicating reaction through a protonated species, is found also. The products of the reactions of chlorine acetate and of chlorine with *trans*-1-nitro-2-phenylethylene are described also.

ISRAEL, SOPER, and their co-workers[2] have shown from studies of the kinetics of the reaction between aqueous hypochlorous acid and a number of relatively reactive olefinic compounds that the hypochlorous acid molecule itself is a relatively unreactive source of electrophilic chlorine. At high concentrations, it can provide the more reactive species chlorine monoxide (ClOCl); and

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[1] Part XI, P. B. D. de la Mare, M. A. Wilson, and M. J. Rosser, *J.C.S. Perkin II*, 1973, 1480.

[2] K. D. Reeve and G. C. Israel, *J. Chem. Soc.*, 1952, 2327; D. A. Craw and G. C. Israel, *ibid.*, p. 550; G. C. Israel, J. K. Martin, and F. G. Soper, *ibid.*, 1950, 1283.

in the presence of acetic acid a kinetic term can be identified consistent with chlorination through chlorine acetate (ClOAc). When mineral acid is added, kinetic terms dependent on the acidity of the medium are found, and are consistent with chlorination through the related protonated forms (*e.g.*, $ClOH_2^+$).[3] The presence of chloride ions in the reaction medium results in reaction through molecular chlorine.

Early speculations [4] that chlorine acetate is responsible for the formation of acetoxy-chlorides when olefinic substances react with molecular chlorine in acetic acid were made most improbable [5] by the kinetic work of Robertson and his co-workers.[6] The conditions under which reactions through chlorine acetate become effective have now been reported for aromatic substitutions.[7,8] These investigations have only recently been extended to additions; it has been shown that the reactions of various derivatives of cinnamic acid with chlorine acetate in acetic acid, and with hypochlorous acid in aqueous acetic acid, give products different from those initiated by molecular chlorine under the same conditions. Different ratios of the diastereoisomeric acetoxy-chlorides are formed (together, for chlorine, with the corresponding dichlorides). A number of these reactions were found to be too fast for convenient kinetic measurement; in this paper, results are reported for the kinetics of addition of chlorine acetate (formed from hypochlorous acid in aqueous acetic acid), to methyl *p*-nitro- and *p*-chloro-*trans*-cinnamate; to 1-nitro-2-phenylethylene, and to acrylic acid. They establish the identity of the main chlorinating species, namely molecular chlorine acetate. The products of addition of chlorine acetate and of chlorine to 1-nitro-2-phenylethylene are described also. A preliminary account of some of this work has already been given.[9]

EXPERIMENTAL

Some of the materials and methods have been described in earlier papers,[1,7,8] and in references therein cited. *trans*-1-Nitro-2-phenylethylene, recrystallised from n-hexane, had m.p. 57° (lit.,[10] 57°). Acrylic acid was a commercial sample (B.D.H.), which was distilled before use; b.p. 141—142° at 760 mmHg (lit.,[11] 140°), purity >99% as estimated from the ^1H n.m.r. spectrum in $CDCl_3$. Solvents are specified as mixtures by volume. For chlorinations in aqueous acetic acid, a solution of hypochlorous acid was prepared from freshly precipitated mercuric oxide and chlorine in the usual way, and reaction was initiated by adding a suitable volume of this to a solution of the olefinic compound in acetic acid. For the few chlorinations measured in acetic acid, a vacuum-distilled solution of chlorine acetate in acetic acid, prepared from mercuric acetate and chlorine in acetic acid,[7] was used. Kinetic measurements were carried out in brown bottles maintained in a thermostat at 25.0°. Aliquot portions were removed at intervals and added to aqueous KI for titration. Some of the most rapid reactions were carried out in V tubes by means of which the reactants could be mixed rapidly at thermostat temperature, and the whole contents of the tube could be quenched by the addition of aqueous KI.

Rate coefficients, which were sensibly constant except where otherwise noted, were calculated by using the second-order formula derived from the rate equation: $-d[ClOR]/dt = k_2[S][ClOR]$, where [ClOR] refers to the total concentration of titratable chlorinating species (referred to elsewhere as ' chlorine acetate '), and [S] to the concentration of the substrate. They are estimated to be reliable to ±5%. The following is an example of a typical kinetic run, with initial concentrations [methyl *p*-nitro-*trans*-cinnamate], 0.100M, [ClOR], 0.259M, [NaOAc], 1.0M. Aliquot parts (5 ml) were removed for titration with 0.0100M-$Na_2S_2O_3$.

Time/10^3 s	1.17	1.43	2.26	3.16	4.04	5.12	5.99	6.27	7.16
Titre/ml	24.92	24.68	24.22	23.60	23.04	22.50	22.04	21.92	21.50
10^3k_2/l mol^{-1} s^{-1}	3.50	3.67	3.25	3.37	3.43	3.37	3.43	3.42	3.47

Mean k_2 3.43 l mol^{-1} s^{-1}.

TABLE 1

Rates of reaction of methyl *p*-nitro-*trans*-cinnamates with ' chlorine acetate ' in acetic acid with and without added water and electrolytes at 25.0°

Water	Reactant concentrations		Added electrolyte	10^3k_2/
(%)	[ClOR]/M	[S]/M	[concentration/M]	l mol^{-1} s^{-1}
0	0.0096	0.0096		**118** [a]
2	0.0157	0.00575		8.7
5	0.0149	0.00575		9.0
10	0.0043	0.00575		5.5
15	0.0138	0.00575		6.0
15	0.00905	0.00550		5.2
20	0.0139	0.0077		5.0
20	0.0137	0.00550		5.8
25	0.0133	0.0107		4.3 [b]
25	0.0095	0.0107		4.8 [b]
25	0.0425	0.0104		4.3
25	0.0129	0.0089		4.7 [b]
25	0.0230	0.0100	NaOAc [0.50]	4.0
25	0.0259	0.0100	NaOAc [1.00]	3.5
25	0.0232	0.0127	$LiClO_4$ [0.25]	7.0
25	0.0259	0.0063	$LiClO_4$ [0.50]	9.5
25	0.0055	0.0060	$HClO_4$ [0.11]	6.3
25	0.0141	0.0063	$HClO_4$ [0.23]	7.8
25	0.0158	0.0070	$HClO_4$ [0.45]	13.0
25	0.00578	0.0107	$AgClO_4$ [0.0028]	7.3 [c]

[a] Highest value obtained; results reproducible only with the same batch of acetic acid, because of influence of trace amounts of water; see Discussion section. [b] Chlorinating agent supplied as chlorine acetate in acetic acid. [c] Initial value is quoted; rate coefficients rose with progress of the reaction; see Discussion section.

In Table 1, the results of additions to methyl *p*-nitro-*trans*-cinnamate in acetic acid and in acetic acid containing

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[3] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1954, 3910.

[4] W. Bockemuller and F. W. Hoffmann, *Annalen*, 1935, **519**, 165.

[5] P. B. D. de la Mare and R. Bolton, ' Electrophilic Additions to Unsaturated Systems,' Elsevier, 1966, pp. 75—108.

[6] I. K. Walker and P. W. Robertson, *J. Chem. Soc.*, 1939, 1515; E. P. White and P. W. Robertson, *ibid.*, p. 1509; P. W. Robertson, R. M. Dixon, W. G. M. Goodwin, I. R. McDonald, and J. F. Scaife, *ibid.*, 1949, 294; L. D. Swindale, B. E. Swedlund, and P. W. Robertson, *ibid.*, 1950, 812.

[7] P. B. D. de la Mare, A. D. Ketley, and C. A. Vernon, *Research*, 1953, **6**, 12S.

[8] P. B. D. de la Mare, I. C. Hilton, and C. A. Vernon, *J. Chem. Soc.*, 1960, 4039; P. B. D. de la Mare, I. C. Hilton, and S. Varma, *ibid.*, p. 4044.

[9] P. B. D. de la Mare, C. J. O'Connor, M. J. Rosser, and M. A. Wilson, *Chem. Comm.*, 1970, 731.

[10] E. Knoevenagel and L. Walter, *Ber.*, 1904, **37**, 4502.

[11] E. Linnemann, *Annalen*, 1874, **171**, 29.

various proportions of added water, with and without added electrolytes, are summarised. Except where otherwise specified, the chlorinating agent was supplied as a solution of hypochlorous acid in water. The corresponding addition to methyl *p*-chloro-*trans*-cinnamate was very rapid; for reaction in 75% acetic acid (25% water) with reactants initially 0.0060M, the second-order rate-coefficient, k_2, was found to have the value of 0.57 l mol^{-1} s^{-1}.

The similar additions to acrylic acid and to 1-nitro-2-phenylethylene gave the results summarised in Table 2.

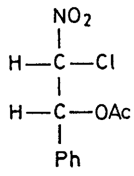
TABLE 2

Rates of reaction of acrylic acid and of *trans*-1-nitro-2-phenylethylene with ' chlorine acetate ' in 76% acetic acid containing 0.01M-$AgClO_4$ at 25°

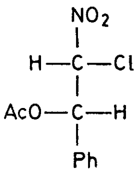
Olefinic compound	Reactant concentrations [ClOR]/M	[S]/M	Added electrolyte [concentration]/M	10^3k_2/l mol^{-1} s^{-1}
CH_2:CH·CO_2H	0.050	0.0036		25
	0.070	0.0036		25
	0.100	0.0036		24
	0.050	0.0036	$HClO_4$ [0.23]	38
	0.050	0.0036	$HClO_4$ [0.46]	51
	0.050	0.0036	$HClO_4$ [0.91]	125
	0.050	0.0036	$HClO_4$ [1.37]	253
	0.050	0.0036	$HClO_4$ [1.60]	348
	0.050	0.0036	$HClO_4$ [1.83]	475
	0.050	0.0036	NaOAc [0.14]	120
	0.049	0.0036	NaOAc [0.36]	265
	0.048	0.0036	NaOAc [0.60]	433
	0.091	0.0036	NaOAc [0.90]	638
	0.0191	0.0036	NaOAc [1.35]	848
	0.0191	0.0036	NaOAc [1.80]	941
	0.050	0.0036	$NaClO_4$ [0.15]	34
	0.050	0.0036	$NaClO_4$ [0.45]	50
	0.050	0.0036	$NaClO_4$ [0.60]	100
PhCH:$CHNO_2$	0.050	0.0025		4.2
	0.050	0.0025		4.4
	0.090	0.0024		4.3
	0.050	0.0023	$HClO_4$ [0.46]	9.3
	0.050	0.0028	$HClO_4$ [0.91]	13.8
	0.040	0.0040	$HClO_4$ [1.37]	37.5
	0.050	0.0041	$HClO_4$ [1.60]	75
	0.050	0.0041	$HClO_4$ [1.83]	154
	0.050	0.0041	$NaClO_4$ [0.15]	4.8
	0.050	0.0041	$NaClO_4$ [0.38]	5.6
	0.050	0.0042	$NaClO_4$ [0.60]	6.6

The products of addition of chlorine acetate to *trans*-1-nitro-2-phenylethylene were recovered after reaction in acetic acid with initial concentrations 0.1M. The solvent was removed under reduced pressure. The presence of the expected diastereoisomeric 1-acetoxy-2-chloro-2-nitro-2-phenylethanes was evident, and no other products were detected, from the ^{1}H n.m.r. spectrum. This contained signals which are attributed for reasons presented in the Discussion section to the adducts conveniently described respectively as the ' *erythro* '- and ' *threo* '-acetoxy-chlorides (1) and (2) respectively, *viz.* for (1), τ ($CDCl_3$) 8.00 (3H, s, OAc), 3.96 (1H, d, *J* 8.5 Hz), 3.72 (1H, d, *J* 8.5 Hz), and 2.60 (5H, s, aromatic H); and for (2), τ 7.92 (3H, s, OAc), 3.96 (1H, d, *J* 5.0 Hz), 3.52 (1H, d, *J* 5.0 Hz), and 2.62 (5H, s, aromatic H). Chromatography of the mixture on silica gel (Kieselgel S, Riedel de Haen), benzene being used as eluant, gave partial separation of the above diastereoisomers, and confirmed the association of the relevant signals. From the original ^{1}H n.m.r. spectrum, the product mixture comprised (1) 56%; (2) 44%.

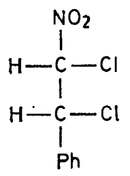
Examination of the ^{1}H n.m.r. spectrum of the products of the similar reaction of molecular chlorine under the same conditions showed the presence of the same two acetoxy-chlorides, now present, however, in the ratio (1) : (2) = 6 : 1. These comprised 28% of the total product; the remaining 72% consisted of the corresponding *erythro*- and *threo*-dichlorides (3) and (4) respectively, in the ratio 2 : 1. The individual ^{1}H n.m.r. spectra could be extracted from the spectrum of the mixture to be represented by signals for (3) at τ ($CDCl_3$) 4.64 (1H, d, *J* 10 Hz, H-1) and 3.92 (1H, d, *J* 10 Hz, H-2); and for (4) at τ 4.38 (1H, d, *J* 6.0 Hz, H-1) and 3.89 (1H, d, *J* 6.0 Hz, H-2). The aromatic signals at τ 2.6 overlapped and formed an unresolved singlet on our instrument. Separation of the dichlorides was effected on silica gel, and gave oils whose separate ^{1}H n.m.r. spectra confirmed these assignments.



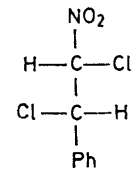
(1) (and its enantiomorph)
' *erythro* '-Acetoxy-chloride



(2) (and its enantiomorph)
' *threo* '-Acetoxy-chloride



(3) (and its enantiomorph)
' *erythro* '-Dichloride



(4) (and its enantiomorph)
' *threo* '-Dichloride

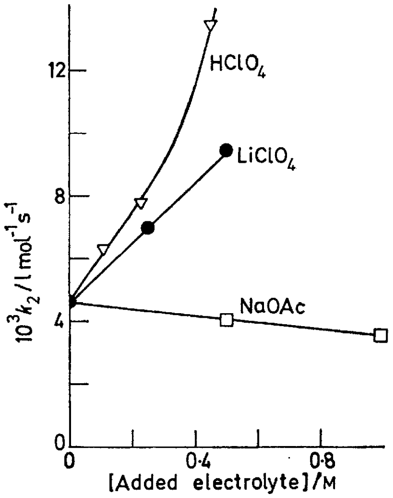


FIGURE 1 Rates of reaction of ' ClOAc ' with methyl *p*-nitro-*trans*-cinnamate in 75% acetic acid at 25°

DISCUSSION

(a) *Kinetics and Products of Chlorination of Methyl* p-*Nitro- and of Methyl* p-*Chloro*-trans-*cinnamate with Chlorine Acetate in Acetic Acid and in Aqueous Acetic Acid*.—The results obtained for addition of chlorine acetate to methyl *p*-nitro-*trans*-cinnamate in aqueous acetic acid (Table 1) correspond well with those obtained for substitutions in aromatic compounds with the same reagent.[8] The rate of addition is not affected by whether the bulk chlorinating species is supplied as hypochlorous acid in water or as chlorine acetate in acetic acid, confirming that under these circumstances the rate of formation of chlorine acetate does not become rate limiting. In Figure 1, the rate of addition is plotted against the concentrations of added acid, base, and salt for reactions in 75% acetic acid. The results make it clear that the main chlorinating species under essentially neutral conditions (*i.e.*, with no added mineral acid) is a molecular reagent. This can be identified as chlorine acetate (ClOAc), since hypochlorous acid would certainly be ineffective under these conditions; molecular chlorine is not present and has been shown [1] to give a different ratio of acetoxy-chlorides in these and related conditions; and reaction through chlorine monoxide would give a kinetic form involving a term in [ClOR]^2, which is not found.

In aqueous acetic acid, the bulk source of electrophilic chlorine is hypochlorous acid. It was estimated previously [8] that the equilibrium constant, [ClOAc][H_2O]/[ClOH][HOAc], is *ca.* 0.0025 in aqueous acetic acid. It is unlikely that this value is independent of the solvent composition; but if it is used to calculate approximate values of the true second-order rate coefficients, k_2^{ClOAc}, for addition of chlorine acetate to methyl p-nitro-*trans*-cinnamate in acetic acid containing various amounts of water, the following results are obtained.

H_2O (%)	0	2	5	10	15	20	25
10^3k_2/l mol^{-1} s^{-1}	118	8.7	9.0	5.5	5.6	5.4	4.5
k_2^{ClOAc}/l mol^{-1} s^{-1}	0.12	0.22	0.60	0.78	1.25	1.71	1.90

The rate of reaction increases with the ionising power of the solvent, a result which is consistent with the Hughes–Ingold theory of solvent action applied to a reaction in which two formally neutral molecules become polarised in reaching the transition state.[12] The increase in rate is not as great as in the corresponding aromatic substitutions that have been studied,[8] a result which may perhaps be associated with a greater solvation of the olefinic than of the aromatic ground state.

As for aromatic chlorination by this reagent, the effects of added electrolytes on the rate of addition are relatively large, and probably reflect changes both in the equilibrium constant for formation of and in the rate of chlorination by chlorine acetate. Added perchloric acid has a markedly larger effect than lithium perchlorate, indicating the probable incursion of an acid-catalysed chlorination at high concentrations of acid. Added silver perchlorate did not reduce the rate of addition to this compound, thus confirming that the effective electrophile is not molecular chlorine; but simple second-order kinetics were not found, and the reaction showed mild autocatalysis.

The true second-order rate coefficient, $k_2^{\mathrm{Cl_2}}$, for the chlorination of methyl p-nitro-*trans*-cinnamate by molecular chlorine in acetic acid [13] has the value 8.2×10^{-5} l mol^{-1} s^{-1}, so chlorine acetate under these conditions is more than a thousand times more reactive than molecular chlorine with this compound. Comparison of the rates of reaction of methyl p-chloro- and methyl p-nitro-*trans*-cinnamate with ‘ chlorine acetate ’ in 75% acetic acid gives a rate ratio of 126, and this result confirms that the reaction of molecular chlorine acetate, like that of molecular chlorine, involves electrophilic attack on the olefinic compound. The corresponding ratio for molecular chlorination of derivatives of cinnamic acid [14] is 490. This comparison fits qualitatively with results for aromatic substitution,[8] where the response of reactivity to change in structure is substantial both for chlorine acetate and for molecular chlorine, but is less for the former reagent.

These kinetic results help to confirm the conclusions derived from our previous account of the products of addition to these cinnamates.[1]

(b) *Kinetics of the Reaction of* 1-*Nitro*-2-*phenylethylene with Chlorine Acetate in Aqueous Acetic Acid.*—By analogy with the corresponding reaction of molecular chlorine, 1-nitro-2-phenylethylene ($k_2^{\mathrm{Cl_2}} = 3.5 \times 10^{-4}$ l mol^{-1} s^{-1}) [15] should react with chlorine acetate a little more rapidly than methyl p-nitro-*trans*-cinnamate does. In fact, it was found to react at about the same rate. The reaction was studied in the presence of silver perchlorate, which in this case did not introduce any kinetic complications, to provide an example confirming that molecular chlorine is not concerned in these reactions. The results (Table 2) are presented graphically in Figure 2. The behaviour is similar to that observed for the corresponding reaction of methyl p-nitro-*trans*-cinnamate. In the absence of added mineral acid, a neutral chlorinating species appears to be under observation, and the rate of reaction is increased by the presence of added sodium perchlorate. At high concentrations of perchloric acid, acid catalysis is evident, and the rate increases more rapidly than the stoicheiometric acidity. The reaction could not be studied satisfactorily in the presence of sodium acetate, probably because the products were unstable to base.

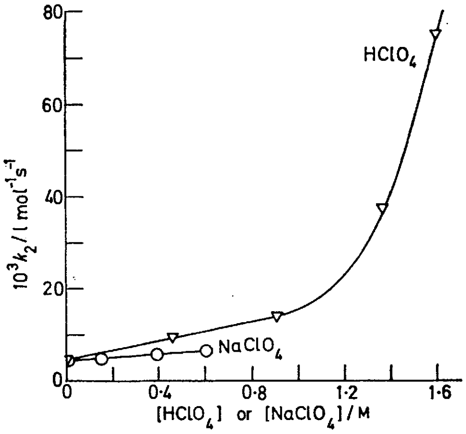


FIGURE 2 Rates of reaction of ‘ ClOAc ’ with 1-nitro-2-phenylethylene in 76% acetic acid containing 0.01M-$AgClO_4$ at 25°

These kinetic results confirm and amplify the kinetic

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[12] E. D. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 763.

[13] I. Hartman and P. W. Robertson, *J. Chem. Soc.*, 1945, 891.

[14] P. B. D. de la Mare, *J. Chem. Soc.*, 1960, 3823.

[15] I. Ting and P. W. Robertson, *J. Chem. Soc.*, 1947, 628.

conclusions reached from study of the reactions of methyl *p*-nitro-*trans*-cinnamate in the absence of silver perchlorate. Since with chlorine acetate the two compounds are of similar reactivity, it appears that the correlation of rate with structure is not perfect; as has been observed also for comparisons of chlorination by molecular chlorine and by hypochlorous acid and perchloric acid in aqueous dioxan.[16]

(c) *Products of Addition of Chlorine and of Chlorine Acetate to* trans-1-*Nitro*-2-*phenylethylene in Acetic Acid*.—These reactions were studied in anhydrous acetic acid, to avoid complications arising from the formation of chlorohydrins. It is assumed that molecular chlorine acetate is involved here also, since in other systems the product compositions are not sensitive to the addition of acid or of base to the medium.[1] The assignment of the stereochemistry of the products has been made on the basis of the generalisation used by a number of workers in this field [1,17,18] that, for compounds of the type PhCH(Cl)·CH(Cl)R and PhCH(OAc)·CH(Cl)R, the '*erythro*'- can be distinguished from the corresponding '*threo*'-diastereoisomer because it has a higher value of the ^{1}H n.m.r. coupling constant, $J_{1,2}$. Formal proof that this is so has been forthcoming for a number of examples, but has not been provided in this instance. The uncertainties inherent in this method of stereochemical assignment have been discussed by us [19] and by others.[17,18] Since for R = CO_2H and CO_2Me the generalisation has been confirmed fully,[18] it seems reasonable to assume that it would apply in the present example (R = NO_2), since the nitro- and the carboxy-group have similar geometries and polar character.

The assignment can be supported also on mechanistic grounds. In Table 3 the compositions of the product mixtures obtained in these additions are summarised, the assignments of stereochemistry having been made on the above basis.

TABLE 3

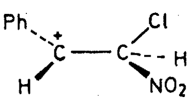
Products of chlorination of *trans*-1-nitro-2-phenylethylene in acetic acid at 25°

Electrophile	Product proportions (In parentheses, stereochemistry of the addition process leading to each product)			
	Dichlorides		Acetoxy-chlorides	
	'*erythro*'	'*threo*'	'*erythro*'	'*threo*'
Cl_2	0.48 (*anti*)	0.24 (*syn*)	0.24 (*anti*)	0.04 (*syn*)
ClOAc			0.56 (*anti*)	0.44 (*syn*)

First, it is to be noted that none of the reactions is stereospecific. A similar lack of stereospecificity for most additions initiated by electrophilic chlorine to phenyl-substituted ethylenes [1,17,18] reflects among other things the fact that the entering chlorine substituent acts only rather ineffectively as a 'neighbouring' or 'bridging' group when the developing carbocationic centre can be stabilised by the phenyl group and the solvent.

Of the reactions under observation, the one expected by analogy with the related cases of the substituted cinnamates [1,18] to show *anti*-stereochemistry most clearly is the addition initiated by electrophilic chlorine to form the acetoxy-chloride, since the entering electrophile tends to direct the nucleophile to the far side of the double bond. Indeed this is found to be the most stereoselective process, and it gives mostly the isomer deduced from its ^{1}H n.m.r. spectrum to be the '*erythro*'-isomer, the product of *anti*-addition to a *trans*-disubstituted ethylene.

Following from this structural confirmation, we conclude that addition of molecular chlorine to form the dichlorides gives the *anti*- with a substantial proportion of the product of *syn*-addition. Addition of chlorine acetate gives acetoxy-chlorides in a ratio very different from that in which these same products are formed from molecular chlorine in the same solvent. Different intermediates must therefore be involved. These results are consistent with the formulation given previously,[1] in which it is considered that chlorine acetate acts as a relatively effective source of nearly free positive chlorine to give in the present case the carbocation having structure approximated in (5). This intermediate is rather indiscriminate in its reaction with solvent. Molecular chlorine, on the other hand, gives first the intermediate (6), still retaining the chloride ion covalently bound in its structure; no-bond resonance with structure (7) may help to stabilise this intermediate. This by dissociation and internal capture of chloride ion is responsible for the formation of the '*threo*'-dichloride (*syn*-addition), and by reaction with solvent gives mainly the '*erythro*'-acetoxy-chloride (*anti*-addition).



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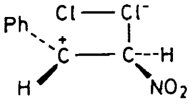

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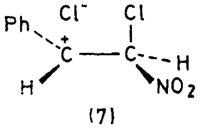

(7)

(d) *Kinetics of Addition of Chlorine Acetate to Acrylic Acid in Aqueous Acetic Acid*.—The kinetics of addition of chlorine acetate to acrylic acid have been investigated only in outline. Aqueous (76%) acetic acid was used as the solvent, and silver perchlorate was included in the medium to prevent reaction through molecular chlorine. Satisfactory second-order kinetics were found, but study of the effects of added electrolytes showed clearly that the reaction takes a course different from that taken by the other substrates. Some of the results are presented graphically in Figure 3.

The powerful catalytic effect of sodium acetate establishes that there is a relatively rapid reaction through the acrylate ion. From the curve of rate against concentration of base, it appears that acrylic acid is nearly com-

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[16] G. W. Burton, P. B. D. de la Mare, L. Main, and B. N. B. Hannan, *J.C.S. Perkin II*, 1972, 265.

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pletely converted into the acrylate ion at *ca.* 2M-NaOAc in 76% acetic acid, when the second-order rate coefficient for reaction with ‘ chlorine acetate ’ (k_2) levels out at *ca.* 1 l mol^{-1} s^{-1}. From this, with the dissociation constant of acrylic acid (K_a/mol dm^{-3} = 5.5 × 10^{-5}),[20] and an estimate of the hydrogen-ion concentration in 76% acetic acid (*ca.* 0.02M),[21] the contribution of reaction through the acrylate ion without additives can be calculated to be no more than *ca.* 10% of the measured rate. Even if this calculation is regarded as quite uncertain, since solutions in 76% acetic acid are likely to be far from ideal, it seems clear (looking also at the rate in the presence of perchloric acid) that the rate coefficient for the reaction of the acrylic acid molecule with ‘ chlorine acetate ’ in 76% acetic acid containing 0.01M-AgClO$_4$ has a value of k_2 = *ca.* 20 × 10^{-3} l mol^{-1} s^{-1}. This is of the order of magnitude expected from the rate of chlorination by molecular chlorine;[5,22] with the latter reagent, acrylic acid reacts about four times faster than methyl *p*-nitro-*trans*-cinnamate does.

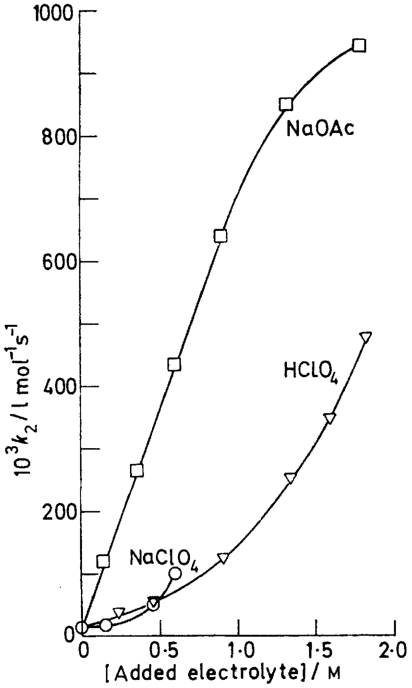

FIGURE 3 Rates of reaction of ‘ ClOAc ’ with acrylic acid in 76% acetic acid containing 0.01M-AgClO$_4$ at 25°

The products of addition of hypochlorous acid to acrylic acid have not been studied in the course of this work, since the stereochemistry would here not have been distinguishable. It is interesting to note, however, that the reaction does not appear to be completely regiospecific; Melikoff[23] has recorded that both 2-chloro-3-hydroxy- and 3-chloro-2-hydroxy-propanoic acid can be isolated from the reaction mixture.

[4/2695 *Received, 23rd December,* 1974]

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