requires as input the difference between the ^2H coupled and decoupled carbon widths and the J coupling constant between the C_2 carbon and bonded deuterium. This coupling constant is 35 Hz. One obtains a $(T_1)^{-1}$ value equal to $\sim$320 sec^{-1}. Substituting this value in eq 3 gives a value of 5×10^{-10} sec for τ_c. This is within a factor of 3–4 that estimated from the ^{13}C T_1 times. A similar type of argument applies to glycine (Figure 6) where we infer from the partially resolved multiplet (Figure 7) that T_1^{-1} for the α-deuterium is approximately 120 sec^{-1}. This estimate together with the fact[36] that $e^2qQ/h \sim 165$ kHz implies a τ_c value of $1\text{–}2 \times 10^{-10}$ sec.

In conclusion, we see that a model which assumes anisotropic motion on the resin can explain the nmr results. We deduce that a short correlation time of the order of 1×10^{-9} sec or less at room temperature determines the T_1 and H values. The line widths, or T_2 values, are determined by a long correlation time. A "wobbling" motion of the resin lattice may be responsible for this long correlation time. It would have been of some interest to study the T_2 ratios of the deuterated and protonated amino acids as a function of temperature to see if this ratio could be increased from 3 to 10 or 15 with increasing temperature. Unfortunately, we did not have a suitable temperature probe for this type of study. The model we propose is a first approximation. Previous work[27,28] done on molecules adsorbed on surfaces supports its basic features. However, the previous studies also revealed features of considerably greater complexity.[27] For example, instead of one short and one long correlation time determining T_1 and T_2, respectively, these studies show a distribution of short and long correlation times.

Acknowledgment. This work was supported by U. S. Public Health Service Grants No. GM 14313-03 to H. Sternlicht and AM 13529-02 to G. L. Kenyon. One of us (E. L. P.) wishes to thank Dr. A. D. McLaren, Professor of Soil Biochemistry, for a number of helpful discussions on surface adsorption. Dr. W. Horsley provided occasional technical assistance, and his help is gratefully acknowledged. We also wish to thank Dr. D. E. Woessner for several clarifying discussions.

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(37) J. A. Pople, *Mol. Phys.*, 1, 168 (1958).

The Kinetics of Iodination of Sodium Phenylpropiolate

Mary H. Wilson[1] and Ernst Berliner[2]

Contribution from the Marion Edwards Park Laboratory of Bryn Mawr College, Bryn Mawr, Pennsylvania 19010. *Received April 25, 1970*

Abstract: The addition of iodine to sodium phenylpropiolate was studied in aqueous solution. At moderate iodide ion concentrations the reaction was found to be termolecular, involving iodine, iodide ion, and sodium phenylpropiolate with an activation energy of 15.3 kcal/mol, and an activation entropy of −23.5 eu. Analysis of the rate constants at low iodide ion concentrations revealed a three-term expression $k_{\text{obsd}} = k_t(I^-)/(K_I + I^-) + k'/(K_I + I^-) + k''/(I^-)(K_I + I^-)$. In this expression k_t is the rate constant for the termolecular reaction, k' the rate constant for a bimolecular reaction involving molecular iodine, and the constant k'' is the rate constant for a reaction possibly involving the hydrated iodine cation (H_2OI^+). K_I is the equilibrium constant for the triiodide ion. Product analyses, salt effects, the relative rates of reaction of phenylpropiolic acid and its anion, the effect of pH, activation parameters, and solvent isotope effects were investigated and are not inconsistent with the proposed mechanism.

The kinetics of the addition of iodine to sodium phenylpropiolate in water was studied in 1933 by Moelwyn-Hughes and Legard.[3] These authors found that at most concentrations the reaction was first order in sodium phenylpropiolate and triiodide ion, which they assumed to be the active iodinating species at high iodide ion concentrations. At low concentrations ($I_2 \leqq 0.0025$ M) the rate of the reaction increased sharply, and they proposed hypoiodous acid as the predominating species. Calculations of the rate constants at two different low iodide ion and iodine concentrations gave results consistent with this proposal.

The early authors kept the ratio of concentrations of sodium phenylpropiolate, iodine, and potassium iodide constant throughout all the experiments (1:1:4) and thus were unable to study the effect of each of these independently of the others. They did not study the effect of added salts, the nature of the products, or the pH dependence of the reaction, which is particularly important if HOI were involved at low iodide ion concentrations. In view of the current interest in additions to acetylenic compounds,[4,5] it seemed worthwhile to study the reaction in greater detail, particularly since it seemed that the reactive species at low concentrations had not been sufficiently identified by the early authors.

Results

The Order of the Reaction. The rate of the reaction is first order with respect to both sodium phenylpropiolate (A) and stoichiometric iodine and the experi-

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(1) Taken in part from the Ph.D. Dissertation of M. H. Wilson, Bryn Mawr College, May 1970; National Science Foundation Trainee, 1967–1968; United States Steel Fellow in Chemistry, 1968–1970.

(2) To whom inquiries should be addressed.

(3) E. A. Moelwyn-Hughes and A. R. Legard, *J. Chem. Soc.*, 424 (1933).

(4) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966.

(5) R. C. Fahey, *Top. Stereochem.*, 3, 237 (1968).

mental rate law is $-d(I_2)_T/dt = k_{obsd}(A)(I_2)_T$. The phenylpropiolate ion concentration was varied by a factor of 7.5 and the concentration of iodine by a factor of 20 (Table I). Runs were conducted at a constant iodide ion concentration. Because of salt effects (see below), the runs in which phenylpropiolate ion concentration was varied were carried out at varying ionic strength without added salts. Sodium phenylpropiolate does not give rise to a salt effect in the concentration range used, but runs in which the ionic strength was kept constant (KNO_3) showed decreasing rate constants with increasing concentration of A.

Table I. Dependence of the Rate on the Concentration of Reactants

Sodium phenylpropiolate, *M*	Iodine, *M*	KI, *M*	μ	$k_{obsd} \times 10^3$, l./mol sec
0.0400	0.0249	0.100	0.140	1.36
0.0400	0.0249	0.100	0.140	1.36
0.1002	0.0248	0.100	0.200	1.35
0.1002	0.0247	0.100	0.200	1.38
0.2000	0.0246	0.100	0.300	1.39
0.2000	0.0244	0.100	0.300	1.38
0.3001	0.0240	0.100	0.400	1.38
0.2998	0.0239	0.100	0.400	1.34
0.1000	0.0025	1.00	1.10	1.52
0.1000	0.0025	1.00	1.10	1.55
0.1000	0.0124	1.00	1.10	1.54
0.1000	0.0124	1.00	1.10	1.54
0.1000	0.0248	1.00	1.10	1.53
0.1000	0.0248	1.00	1.10	1.54
0.1000	0.0495	1.00	1.10	1.53
0.1000	0.0494	1.00	1.10	1.52
0.0400	0.0251	0.100	0.500[a]	1.66
0.0400	0.0250	0.100	0.500[a]	1.62
0.0750	0.0247	0.100	0.500[a]	1.61
0.0750	0.0247	0.100	0.500[a]	1.58
0.1500	0.0247	0.100	0.500[a]	1.53
0.1500	0.0248	0.100	0.500[a]	1.48
0.3000	0.0239	0.100	0.500[a]	1.40
0.3000	0.0244	0.100	0.500[a]	1.37

[a] Kept constant with KNO_3.

The Effect of Added Salts. Small salt effects were observed with all added salts other than sodium phenylpropiolate. At both high and low iodide ion concentrations the salt effects are nonlinear with respect to concentrations but nearly linear with respect to the square root of the concentration of added salts (Table II, Figure 1). The values for 1.10 *M* concentrations of KI and NaI demonstrate that the identity of the cation is unimportant. Also, these two salts have a somewhat smaller effect than NaCl, KNO_3, or $NaClO_4$.

The Effect of Iodide Ion. At high iodide ion concentrations (0.02–0.10 *M*) in the region where salt effects are not important, the rate of the reaction is independent of the concentration of iodide ion (Table III), as found earlier.[3] In runs at low iodide ion concentrations (0.01–0.00075 *M*) the rate constants increase with a decrease in iodide ion concentration as found by Moelwyn-Hughes and Legard.[3] A straight line results when rates are plotted against $1/(I^-)_{fr}(K + I^-_{fr})$ (Figure 2), where I^-_{fr} represents the free iodide ion concentration and K_I the dissociation constant of the triiodide ion, which was taken as 1.55×10^{-3} at 30°.[6] The concentrations of free iodine and iodide were calculated from known equations.[3]

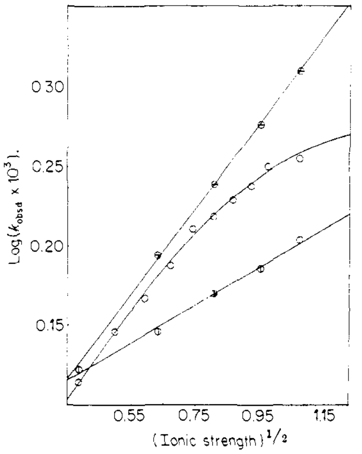

Figure 1. Dependence of the rate on ionic strength: ⊖, $NaClO_4$; O, KNO_3; ⦶, NaI.

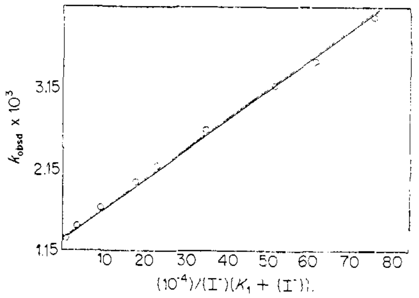

Figure 2. Dependence of the rate on iodide ion concentration.

The Effect of pH. The nature of the pH dependence of the low and high iodide reactions was investigated in the pH range 3.6–7.3 with acetate and phosphate buffers (Table IV). The concentration of the undissociated acid is 3% or less in this range. The high iodide reaction was not expected to exhibit a dependence on the hydrogen ion concentration. Yet, in acetate buffers, there is a linear decrease in rate with increasing concentration of hydrogen ions (HAc). The magnitude of this effect decreases with a decrease in buffer concentration, which suggests that a medium effect caused by the acetic acid is responsible. When the acetic acid concentration varies from 1.0 to 0.01 *M*, the rate constant changes from runs at pH 5.6 to runs at pH 3.6 by 32%. When the acetic acid concentrations are less (from 0.50 to 0.005 *M* and from 0.25 to 0.0025 *M*), the change in rate constants over the same pH range is only 18 and 12% (Figure 3). The trend is the same at low iodide ion concentrations. Since salt concentrations of 0.10 *M* or less have little effect on the rate, the variations in rate are best explained as being due to a medium effect related to the acetic acid concentrations. Support for this explanation is provided by the constancy of rate in phosphate buffers at constant ionic strength in the pH range from 5.4 to 7.3. There is also no indication of general acid–base catalysis. The lack of dependence of rate on pH is true in reactions at both high and low iodide ion concentrations.

The Reaction of the Acid and the Anion. In order to elucidate the electronic nature of the attack on the

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(6) E. N. Rengevich and E. A. Shilov, *Ukr. Khim. Zh.*, **28**, 1080 (1962); *Chem. Abstr.*, **59**, 4590*f* (1963).

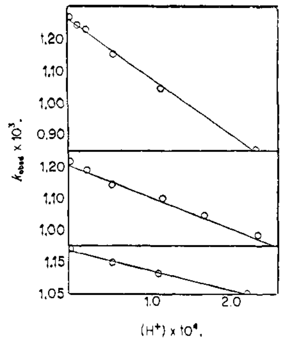

Figure 3. Dependence of the rate on acetate buffers: upper curve, (NaOAc) = 0.10 *M*; middle curve, (NaOAc) = 0.050 *M*; lower curve, (NaOAc) = 0.025 *M*.

triple bond, the relative rates of reaction of the acid and the anion were studied at both high and low iodide ion concentrations. A range of acidities from $H^+ = 4.47 \times 10^{-3}$ to 6.00×10^{-1} *M* was investigated by the addition of HCl. The percentage of dissociation of phenylpropiolic acid varies from 57 to 1% under these conditions. The concentration of reactants was limited by the low solubility of phenylpropiolic acid in water (≃0.20 *M*). Rates decrease with an increase in hydrogen ion concentration. If the rate constant for the iodination of the free acid is k_{HA}, and that for the anion is k_A, the rate should be $-d(I_2)_T/dt = k_{HA}(I_2)_T \cdot (HA) + k_A(I_2)_T(A)$. The concentrations of the acid and the anion are related by $K_A = (H^+)(A^-)/(HA)$ and (A) + (HA) = *C*, where *C* stands for the stoichiometric phenylpropiolic acid concentration and K_A is the dissociation constant of the acid.[7] Therefore, the rate should be given by $-d(I_2)_T/dt = k_{obsd}(I_2)_T(C) = [(k_{HA}(H^+) + k_AK_A](I_2)_T(C)/(K_A + H^+)$ and thus $k_{obsd} = (k_{HA}(H^+) + k_AK_A)/(K_A + H^+)$. A plot of $k_{obsd}(K_A + H^+)$ against (H^+) results in a straight line, from which k_{HA} and k_A can be obtained (Figure 4, Table V). The two rate constants are of the same order of magnitude, but k_A is greater than k_{HA} at both low and high iodide ion concentrations. This implies that the iodinating species is electrophilic. The values of k_A obtained

Table II. The Effect of Added Salts on the Rate

KI, *M*	NaI, *M*	KNO_3, *M*	$NaClO_4$, *M*	μ	$k_{obsd} \times 10^3$, l./mol sec
(A) Sodium Phenylpropiolate = 0.050 *M*, $I_2 \simeq 0.025$ *M*					
0.100		0		0.150	1.30
0.100		0.100		0.250	1.40
0.100		0.200		0.350	1.47
0.100		0.300		0.450	1.54
0.100		0.400		0.550	1.63
0.100		0.500		0.650	1.66
0.100		0.600		0.750	1.70
0.100		0.700		0.850	1.73
0.100		0.800		0.950	1.78
0.100		1.000		1.150	1.80
	0.100			0.150	1.32
	0.350			0.400	1.40
	0.600			0.650	1.48
	0.850			0.900	1.53
	1.100			1.150	1.60
	0.100		0.250	0.400	1.56
	0.100		0.500	0.650	1.73
	0.100		0.750	0.900	1.89
	0.100		1.00	1.150	2.04
1.100[a]				1.200	1.53
	1.100			1.150	1.60
0.100		1.000		1.150	1.80
	0.100		1.000	1.150	2.04
0.100			1.000[b]	1.150	2.35
(B) Sodium Phenylpropiolate ≃ 0.030 *M*, $I_2 \simeq 0.00098$ *M*, KI = 0.0020 *M*					
		0		0.032	3.01
		0.020		0.052	3.04
		0.050		0.082	3.08
		0.100		0.132	3.14
		0.200		0.232	3.20
		0.300		0.332	3.27
		0.400		0.432	3.35

[a] Phenylpropiolate = 0.100 *M*. [b] NaCl.

Table III. Dependence of the Rate on the Iodide Ion Concentration

KI, *M*	$k_{obsd} \times 10^3$, l./mol sec
(A) Sodium Phenylpropionlate ≃ 0.050 *M*, $I_2 \simeq 0.005$ *M*	
0.0200	1.22
0.0300	1.18
0.0500	1.17
0.0800	1.21
0.100	1.22
(B) Sodium Phenylpropiolate ≃ 0.050 *M*, $I_2 \simeq 0.0005$ *M*	
0.0100	1.15
0.0050	1.29
0.0030	1.53
0.0020	1.84
0.0017	2.04
0.0013	2.48
0.0010	3.04
0.00087	3.33
0.00075	3.88
	10.4[a]

[a] Sodium phenylpropiolate = 0.010 *M*.

Table IV. Dependence of the Rate on pH in Phosphate Buffers

KH_2PO_4, *M*	Na_2HPO_4, *M*	KI, *M*		pH	$k_{obsd} \times 10^3$, l./mol sec
(A) Sodium Phenylpropiolate ≃ 0.030 *M*, $I_2 \simeq 0.001$ *M*, μ of buffers = 0.050 *M*					
0.0450	0.0017	0.050		5.36	1.22
0.0333	0.0056	0.050		5.99	1.22
0.0150	0.0117	0.050		6.66	1.22
0.0050	0.0150	0.050		7.27	1.23
0.0450	0.0017	0.0020		5.42	2.33
0.0333	0.0056	0.0020		6.06	2.33
0.0150	0.0117	0.0020		6.74	2.34
0.0050	0.0150	0.0020		7.32	2.33
			KNO_3, *M*	μ	
(B) Sodium Phenylpropiolate ≃ 0.030 *M*, $I_2 \simeq 0.001$ *M*, pH 6.92					
0.0025	0.0075	0.050	0.975	1.08	1.77
0.0050	0.0150	0.050	0.950	1.08	1.77
0.0075	0.0225	0.050	0.925	1.08	1.78
0.0025	0.0075	0.0020	0.975	1.032	2.83
0.0050	0.0150	0.0020	0.950	1.032	2.87
0.0075	0.0225	0.0020	0.925	1.032	2.93

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[7] G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4762 (1956).

Table V. Rate Constants for the Iodination of the Acid and the Anion

KI, M	$k_{HA} \times 10^3$, l./mol sec	$k_A \times 10^3$, l./mol sec
0.050	0.664	1.07
0.0020	0.614	1.61

above agree with the rate constant obtained directly for sodium phenylpropiolate.

At a hydrogen ion concentration of $(H^+) \geqq 0.16\ M$ the above relationship fails and the rates fall off faster than predicted by the equation. For $(H^+) \gg K_A$ a linear dependence of k_{obsd} on $1/(H^+)$ is predicted. Instead, a linear decrease of rate with an increase in hydrogen ion concentration is obtained. This may be due to the formation of a complex between the triple bond and a proton, which renders the complexed bond unreactive toward iodine addition. Measurements at this pH were not made at a low iodide ion concentration.

Runs were also conducted on the free acid at a constant pH and varying low iodide ion concentrations. The rates are linearly related to $1/(I^-)_{fr}(K_1 + I^-_{fr})$, as they are for the anion, so that the iodinating species is the same for both the free acid and the anion.

The Effect of Temperature. Activation parameters were determined by measuring the reaction rates at 5° intervals from 15 to 40° for the high, and from 15 to 35° for the low iodide reaction (Table VI). Satisfactory straight lines were obtained from least-square plots of log k against $1/T°K$.

Table VI. Dependence of Rate on Temperature

T, °C	$k_{obsd} \times 10^3$, l./mol sec
Sodium Phenylpropiolate $\simeq 0.05\ M$, $I_2 \simeq 0.001\ M$	
(A) KI = 0.050 M[a]	
15.0	0.313
20.0	0.497
25.0	0.766
30.0	1.16
35.0	1.73
40.0	2.64
(B) KI = 0.0020 M[b]	
15.0	0.364
20.0	0.682
25.0	1.18
30.0	2.08
35.0	3.79

[a] $\Delta E_a = 15.3 \pm 0.1$ kcal/mol, log $A = 8.09 \pm 0.05$, $\Delta S^{\ddagger} = -23.5 \pm 0.2$ eu. [b] $\Delta E_a = 20.5 \pm 0.2$ kcal/mol, log $A = 12.08 \pm 0.14$, $\Delta S^{\ddagger} = -5.25 \pm 0.06$ eu.

Solvent Isotope Effects. The solvent isotope effects were measured at high and low iodide ion concentrations. For the former reaction the ratio k_{H_2O}/k_{D_2O} is 1.10 and for the latter it is 1.42.

Product Analysis. Two products were isolated from runs at high iodide ion concentration. The first, α,β,β-triiodostyrene ($C_6H_5CI{=}CI_2$), precipitated from solution in 1.3–2.8% yield based on starting material. The largest yield of this compound was obtained from the oldest reaction mixture. The styrene was identified by comparison with an authentic sample. The major product, α,β-diiodocinnamic acid, was identified by thin layer chromatography, its infrared spectrum, and melting point. The acid is assumed to be the trans isomer, and only one isomer of this acid has ever been synthesized. No indone is formed on heating it with sulfuric acid, whereas an indone is formed with ease from *cis*-dibromocinnamic acid.[8] The liberation of iodine from the acid near its melting point also indicates the trans arrangement, as iodine is eliminated from *trans*- but not *cis*-1,2-diiodoethylene.[9] A single compound with a sharp melting point is produced in the preparative aqueous iodination of sodium phenylpropiolate in the presence and absence of light.[10] The reaction product in the present case can therefore be assumed to be the trans isomer. No detectable amount of products of solvent intervention was found in two of three isolation runs. A barely detectable amount of a keto acid was found in the third. In an isolation run with initial reactant concentrations 0.05 M, the yield of α,β-diiodocinnamic acid was calculated to be 72%; 26% of the starting material was unchanged. The amount of starting material and products recovered averaged 97%.

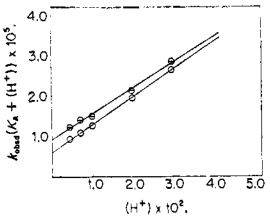

Figure 4. Dependence of the rate on hydrogen ion concentration: ⊖, (KI) = 0.002 M; ○, (KI) = 0.05 M.

In the low iodide runs, the yield of triiodostyrene was considerably greater and increased with decrease in iodide ion concentration. The mixture of acidic products proved difficult to analyze. Product identification was made by analytical and preparative thin layer chromatography and infrared spectra. Gas chromatography could not be used because the products decomposed on the columns. Unreacted phenylpropiolic acid was identified in all product mixtures. Diiodocinnamic acid was found in all runs except in one of two runs without added iodide. The amount of this acid in the second run without iodide was estimated as 5%, and as much as 5% might not have been detected in the former run.

The other main products were keto acids detected as discussed in the Experimental Section. Iodo keto acids would be expected to be formed by the addition of water to an intermediate iodonium or vinyl cation, followed by ketonization, by analogy to such additions in olefinic halogenations.[4,5] Iodine-free keto acids could then be produced through reduction by iodide ion. Three keto acids were formed, separable by thin layer chromatography, but attempts to identify them were rendered difficult by the necessity of working with very small amounts of these acids and by the ease of decomposition of β-keto acids. An extraction of the products with bicarbonate proved the acidity of the compounds, and a reaction and separation with Girard's

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(8) R. Stoermer and P. Heymann, *Chem. Ber.*, **46**, 1249 (1913); A. Glawe, *ibid.*, **35**, 2936 (1902).

(9) S. I. Miller and R. M. Noyes, *J. Amer. Chem. Soc.*, **74**, 3403 (1952).

(10) T. C. James and J. J. Sudborough, *J. Chem. Soc.*, **91**, 1037 (1907).

reagent T furnished further evidence for the presence of carbonyl groups. One of the keto acids appeared to be completely enolic on the thin layer plate, because it did not give a test with 2,4-dinitrophenylhydrazine. This acid was not detected in runs without added iodide ion.

Tests with authentic samples revealed the absence of detectable amounts of benzoylacetic acid ($C_6H_5COCH_2COOH$) and phenylpyruvic acid ($C_6H_5CH_2COCOOH$), both of which are possible products, as well as benzoic acid, iodoacetic acid, and acetophenone, all of which might be produced from keto acids. Authentic benzoylacetic acid decomposed to give acetophenone under the treatment used to isolate the products, but no acetophenone was found among the products of the reaction. However, several weeks of standing of the isolated product mixture at room temperature did result in a decrease in the amount of keto acids and the apparent formation of acetophenones, probably iodinated acetophenones.

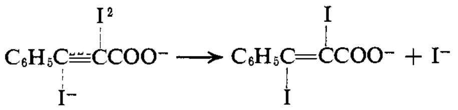
The acids are presumably mono- and diiodinated keto acids, but it was not possible to determine conclusively the presence of iodine in all of them. Attempts to synthesize iodobenzoylacetic acid as a model compound failed. The presence of iodine was confirmed in one of the keto acids and in one of the apparent acetophenones produced by decomposition of a keto acid. The position of the carbonyl group cannot be confirmed in all of the three acids, but one of them must be a β-keto acid because of the presence of an acetophenone among its decomposition products. In runs with identical molar quantities of reactants (0.0008 *M*) the material distribution was calculated as follows: styrene 26%, diiodocinnamic acid 15%, keto acids 35%, and unreacted starting material 26%. In runs without initial iodide the average distribution was 35% styrene, 5% diiodocinnamic acid, 25% keto acids, and 35% unreacted starting material.

Discussion

In all further discussions the concentrations of free molecular species will be represented by enclosure in parentheses; stoichiometric concentrations will be represented by parentheses followed by the subscript T.

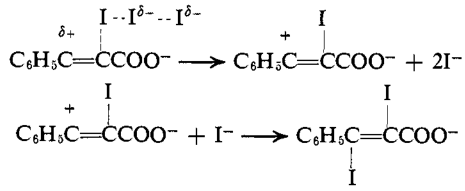
(A) **Reaction at High Iodide Ion Concentrations.** In the range of concentration for which salt effects are negligible, the reaction is independent of the concentration of iodide ions. There are three mechanisms which satisfy the kinetics.

(a) If the mechanism involves iodine and an iodide ion, the rate should be $-d(I_2)_T/dt = k_{obsd}(I_2)(I^-)(A)$. The concentration of free iodine in solution is $(I_2) = K_1(I_2)_T/(K_1 + I^-)$. The rate expression and rate constant for this termolecular reaction should then be $-d(I_2)_T/dt = k_tK_1(A)(I_2)_T(I^-)/(K_1 + I^-)$ and $k_{obsd} = k_tK_1(I^-)/(K_1 + I^-)$. Because $K_1 = 1.55 \times 10^{-3}$, at moderate concentrations of iodide ion, the term $(K_1 + I^-)$ may be reduced to I^-, and the rate constant for the termolecular reaction is given by $k_{obsd} = k_tK_1$, as observed. This reaction may be pictured as in (a).



$$\overset{I^2}{\underset{}{C_6H_5C\equiv C}}COO^- \text{ (with } I^- \text{ below) } \longrightarrow C_6H_5C(I){=}C(I)COO^- + I^- \qquad (a)$$

(b) The second possibility, kinetically indistinguishable from the first, involves the triiodide ion, as shown in (b). For this bimolecular reaction the rate ex-



$$C_6H_5\overset{\delta+}{C}{=}\overset{I\cdots I^{\delta-}\cdots I^{\delta-}}{C}COO^- \longrightarrow C_6H_5\overset{+}{C}{=}\overset{I}{C}COO^- + 2I^- \qquad (b)$$

$$C_6H_5\overset{+}{C}{=}\overset{I}{C}COO^- + I^- \longrightarrow C_6H_5\underset{I}{C}{=}\overset{I}{C}COO^-$$

pression is $-d(I_2)_T/dt = k_b(A)/(I_2)_T(I^-)/(K_1 + I^-)$ and $k_{obsd} = k_b$. This is the mechanism proposed by Moelwyn-Hughes and Legard.[3]

(c) The third possibility involves reversible complexing between the substrate and I_2, followed by rate-determining reaction with external iodide. For this mechanism $k_{obsd} = k_cK_1K_c$, where K_c is the complex equilibrium constant.

In our opinion the termolecular mechanism (a) (Ad_3E) seems most consistent with the data. The data on salt effects are not particularly helpful in distinguishing between the possibilities. Both the bi- and termolecular mechanisms should show similar increases in rate with an increase in ionic strength, as two negative ions are involved in each. Also, the range of concentrations was larger than usual for the limiting law to apply. The small solvent isotope effect is consistent with a mechanism involving no transfer of protons or hydroxyl ions. The effect is small enough to be explained by the change in medium and in the constants for ionic equilibria. The observed lack of dependence on pH is expected for either mechanism.

The most compelling evidence for the termolecular mechanism comes from the product isolation. The failure to detect significant amounts of keto acids makes it very likely that the mechanism is termolecular. The evidence of solvent participation in similar reactions[4,5,11] and the formation of keto acids in the low iodide reaction suggest that solvent participation occurs to a significant extent in the present instance, if the reaction were bimolecular (Ad_2E). An identical mechanism, also based on a combination of kinetic and product data, has been suggested for the bromination of 1-phenylpropyne in the presence of bromide ions.[12,13] Similarly, a study of the elimination of iodine from 1,2-diiodoethylene has indicated that the reverse, the addition of iodine to acetylene, may be a termolecular trans reaction.[9]

The activation energy (15.3 kcal/mol) and entropy (−23.5 eu) are not inconsistent with the suggested termolecular mechanism, and the former agrees with the activation energy found by the earlier workers (15.5 kcal/mol).[3] A termolecular reaction would be expected to have such a low activation entropy, whereas that of a bimolecular reaction should be greater. A similar value of -23 ± 4 eu was calculated for the methanolic iodination of acetylene.[9]

We have not overlooked the possibility that in the termolecular reaction the attack might be initiated by the iodide ion[14] or that bond making at the two acetyle-

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(11) R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, 90, 2124 (1968); 88, 5555 (1966).

(12) J. A. Pincock and K. Yates, *ibid.*, 90, 5643 (1968).

(13) See also ref 11 for the termolecular trans addition of hydrogen chloride to 3-hexyne.

(14) For instance, G. F. Dvorko and D. F. Mironova, *Ukr. Khim.*

Table VII. Calculated Contributions of the Three Reactions[a]

k_{obsd}, l./mol sec	$(I_2)_T$, M	$(I^-)_T$, M	$k_tK_1(I^-)/[K_1 + I^{2-}]$	$k'K_1/[K_1 + I^-]$	$k''/(I^-)[K_1 + I^-]$	k_{calcd}, l./mol sec
3.88×10^{-3}	0.00050	0.000750	3.27×10^{-4}	9.35×10^{-4}	2.62×10^{-3}	3.88×10^{-3}
3.33×10^{-3}	0.00050	0.000875	3.64×10^{-4}	8.91×10^{-4}	2.13×10^{-3}	3.38×10^{-3}
3.04×10^{-3}	0.00050	0.001000	3.99×10^{-4}	8.48×10^{-4}	1.77×10^{-3}	3.02×10^{-3}
2.48×10^{-3}	0.00050	0.001300	4.77×10^{-4}	7.65×10^{-4}	1.20×10^{-3}	2.44×10^{-3}
2.04×10^{-3}	0.00050	0.001700	5.58×10^{-4}	6.70×10^{-4}	7.90×10^{-4}	2.02×10^{-3}
1.84×10^{-3}	0.00050	0.002000	6.07×10^{-4}	6.16×10^{-4}	6.11×10^{-4}	1.83×10^{-3}
1.53×10^{-3}	0.00050	0.003000	7.22×10^{-4}	4.85×10^{-4}	3.18×10^{-4}	1.52×10^{-3}
1.29×10^{-3}	0.00050	0.005000	8.61×10^{-4}	3.27×10^{-4}	1.21×10^{-4}	1.31×10^{-3}
1.15×10^{-3}	0.00050	0.01000	9.89×10^{-4}	1.82×10^{-4}	0.33×10^{-4}	1.20×10^{-3}
1.16×10^{-3}	0.00100	0.05000	1.15×10^{-3}	0.04×10^{-3}	0.14×10^{-5}	1.19×10^{-3}
2.02×10^{-3}	0.00100	0.00200	5.65×10^{-4}	6.61×10^{-4}	7.50×10^{-4}	1.98×10^{-3}
	0.02500	0.4000	1.15×10^{-3}	5.3×10^{-6}	10^{-8}	
	0.00080	0.00080	3.14×10^{-4}	9.45×10^{-4}	2.80×10^{-3}	

[a] $k' = (1.30 \pm 0.003) \times 10^{-3}$, $k'' = (3.47 \pm 0.04) \times 10^{-9}$.

nic carbon atoms may not be completely synchronous.[9] The demonstration that $k_A > k_{HA}$ (Table V) indicates that the electrophilic component in the attack predominates. However, the difference between the reactivity of the anion and the acid is not at all large, and that should be typical of a reaction in which both an electrophile and a nucleophile are involved in the rate-controlling step.

(B) Reaction at Low Iodine Ion Concentrations. As shown earlier, the reaction at low iodide ion concentration is proportional to $1/(I^-)(K_1 + I^-)$. If hypoiodous acid were the iodinating species, k_{obsd} should be equal to $k_{HOI}K_1K_2/(H^+)(I^-)(K_1 + I^-)$ where K_2 is the hydrolysis constant of iodine. Although the iodide ion dependence is correct, the reaction is independent of pH, and hypoiodous acid must be ruled out.

It is not possible to explain the observed dependence on iodide ion concentration by assuming only one reaction, or two concurrent reactions. Only if three concurrent reactions are postulated is it possible to account for the kinetic data.

If only one reaction dependent on $1/(I^-)(K_1 + I^-)$ is occurring, the straight line in Figure 2 should pass through the origin. Actually, the intercept is 1.21×10^{-3}. If it is assumed that the termolecular reaction, which is observed at high iodide ion concentration, also contributes, the observed rate constant should be

$$k_{obsd} = k_tK_1(I^-)/(K_1 + I^-) + k'/(I^-)(K_1 + I^-) \quad (1)$$

The first term differs from the one at high iodide ion concentration, because at low iodide the term $(K_1 + I^-)$ does not reduce to I^-. The value of k_tK_1 (1.15×10^{-3}) is known from experiments. Hence, the contribution of the first term in eq 1 may be calculated and subtracted from k_{obsd}. The resulting constant should be linearly dependent on the second term of eq 1, but this is not observed. If, instead, a reaction involving free iodine were involved, the following equation should be valid

$$k_{obsd} = k'K_1/(K_1 + I^-) + k''/(I^-)(K_1 + I^-)$$

but a plot of $k_{obsd}(K_1 + I^-)$ against $1/(I^-)$ yields a curve. If all three reactions are considered, the three-term expression (eq 2) is obtained

$$k_{obsd} = k_tK_1(I^-)/(K_1 + I^-) + k'K_1/(K_1 + I^-) + k''/(I^-)(K_1 + I^-) \quad (2)$$

The contribution of the first term may again be subtracted from this expression to give $k^*(K_1 + I^-) = k'K_1 + k''/(I^-)$. If $k^*(K_1 + I^-)$ is plotted against $1/(I^-)$ a straight line is obtained (Figure 5) and from the least-squares slope and intercept the contributions of each of these reactions to the total rate constant may be calculated for each concentration of (I^-) and I_2, if salt effects are ignored (Table VII). The sum of these contributions agrees well with the observed rate constants.

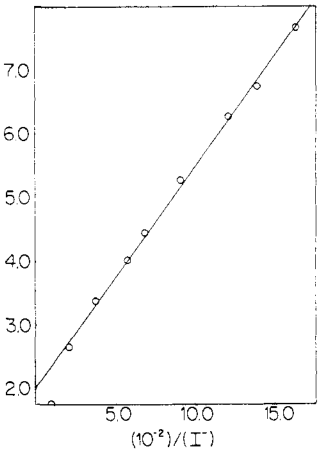

Figure 5. Dependence of the rate on $1/(I^-)$ (eq 2).

According to the data in Table VII, all three terms contribute significantly to the low iodide reaction. However, at the lowest iodide ion concentration (0.00075 M) the third term is preponderant and contributes 67.5% to the total. As the iodide ion concentration increases, the first term assumes more importance at the expense of the other two, and at a 0.05 M iodide ion concentration the first term contributes 96.6, the second 3.36, and the third about 0.1%. At the iodide ion concentrations at which the high iodide runs were conducted, only the first term is important and the other two could not be discovered kinetically.

The rate expression shows that iodination occurs by three paths through transition states of the com-

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Zh., **32**, 362 (1966); *Chem. Abstr.*, **65**, 7014 (1966), and earlier papers by E. A. Shilov and G. F. Dvorko. Also, E. Mauger, Ph.D. Dissertation, Bryn Mawr College, May 1970, unpublished results.

position AI_3^-, AI_2, and AI^+ (see below). There are numerous mechanistic schemes than can be made to account for the kinetics. Not all of them are consistent with the proportions of products formed or with chemical evidence. In the following discussion some likely schemes are considered, as well as some which are kinetically feasible but seem to fall short on other counts. None of them can be completely ruled out, and others can undoubtedly be formulated.

The first term in the three-term equation (eq 2) is the same as the total expression at high iodide ion concentration and presumably also involves a termolecular attack by iodine and iodide. It is mainly responsible for the α,β-diiodocinnamic acid formed at low iodide ion concentration.

The reaction corresponding to the second term in eq 2 involves only free iodine in the first step. The most straightforward mechanistic possibility is a rate-determining attack of free iodine to form a cationic intermediate, followed by a fast reaction with a nucleophile. The rate constant for this reaction, calculated from the intercept in Figure 5, is 1.30×10^{-3} l./mol sec. Product data do not rule out this mechanism, and both iodide and water should compete for the intermediate. The intermediate, either a vinyl cation or a bridged iodonium ion, would only be poorly stabilized and highly reactive, and would not react selectively in preferring one nucleophile over another. The intermediate might conceivably also be reduced by iodide ion to form ultimately keto acids, but no iodine-free keto acids could be discovered among the products.

A variant of this scheme involves a termolecular reaction of A with iodine and water. If the concentration of water is taken to be 55 M, the rate constant for this termolecular reaction is calculated to be 2.36×10^{-5} l.^{2}/mol^2 sec. For the termolecular iodine–iodide reaction the rate constant k_t may be found from the experimental values $k_tK_1 = 1.15 \times 10^{-3}$ and is 7.42×10^{-1} l.^{2}/mol^2 sec. These constants are in the order expected from the relative nucleophilicities of water and iodide ion. Although the presence of the termolecular iodine–iodide reaction makes a termolecular iodine–water reaction an attractive possibility, there is not sufficient evidence to distinguish between the two possibilities for the second term in eq 2.

The kinetic data are also not inconsistent with a fast equilibrium between iodine and A to form the cationic intermediate and iodide ion, followed by a rate-controlling attack of iodide ion. If this were the correct mechanism, two reactions would be occurring simultaneously, one involving a termolecular attack by iodine and iodide (the first term in eq 2), and the other a bimolecular reaction with a *subsequent* attack by iodide. The products of this reaction would be the diiodo acid, or keto acids, if the attack by iodide involved a reduction. If no reduction took place, all of the product would have to be diiodocinnamic acid, but this is not consistent with the amount of diiodo acid isolated.

There are two mechanistic possibilities for the third term in eq 2. One is a slow reaction of the hydrated iodine cation followed by a fast attack of water or iodide ion on the intermediate. The cation is formed by $I_2 + H_2O \rightleftarrows H_2OI^+ + I^-(K_3)$ and $k_{\text{obsd}} = k_{I^+}K_1K_3/(I^-)(K_1 + I^-)$. The mechanism is therefore compatible with the kinetic data. The main product would probably be the keto acids. The concentration of $(H_2OI)^+$ is sufficiently great in solution of low iodide ion concentration for consideration as an iodinating agent. The best value for the dissociation constant K_3 is 1.2×10^{-11} M at 25°.[15] If it is assumed that the value will not be significantly different at 30°, then at a 0.00075 M concentration of iodide ion and 0.0005 M iodine, the concentration of the iodine cation is 7×10^{-12} M. From eq 2 and the slope of the line in Figure 5 ($k_{I^+}K_1K_3 = (3.47 \pm 0.04) \times 10^{-9}$), a rate constant of $k_{I^+} = (1.87 \pm 0.02) \times 10^5$ l./mol sec is obtained for this reaction. This indicates that H_2OI^+ is more reactive than I_2 by a factor of 10^8, which is consistent with the great reactivity expected of this species.

As in the case of aromatic iodination,[16] there is a kinetic ambiguity about the hydrated iodine cation mechanism. The alternate possibility involves a fast equilibrium of the phenylpropiolate anion with iodine, followed by a rate-determining attack by water on the cationic intermediate, or decomposition of the intermediate to triiodostyrene. Conversion to triiodostyrene cannot be the sole fate of the intermediate, because an insufficient amount of the styrene is produced. Rate-determining attack by water on the intermediate should result in the formation of keto acids only, but product isolation data do not allow a distinction between the two mechanisms in this case. The positive iodine mechanism is preferred, because it is hard to see why the reaction of the vinyl cation with water should be rate limiting, and why the presumably unstable and very reactive intermediate should not immediately be captured by the nucleophile before it returns to reactants. Noyce and coworkers were able to demonstrate that the attack of water on a phenylvinyl cation could not be rate controlling in the acid hydration of phenylpropiolic acid.[17] Although the above mechanism is therefore unlikely, it cannot be completely ruled out.[18]

Salt effects, solvent isotope effects, and the ratio of reactivity of the anion to the acid are similar to those in the high iodide reaction. They are difficult to use as mechanistic criteria because in the range of concentrations in which they were studied, all three reactions contribute about equally to the total rate (28.6, 33.4, and 38.0%), making the separate effects on the three reactions, as well as on the preequilibria which may have to be considered for some of them, difficult to sort out. The slightly higher isotope effect (1.41) may simply indicate the greater need for solvation of the positive charge on the intermediate. The greater reactivity of the phenylpropiolate anion relative to the acid in the low iodide reaction (2.62, as compared to 1.61 at high iodide ion concentration) may arise from the stabilization of the cationic intermediate by the carboxylate ion and the absence of a nucleophilic component in the rate-controlling step.

The activation parameters at low iodide ion concentrations ($E_{\text{act.}} = 20.5$ kcal/mol; $\Delta S^{\ddagger} = -5.25$ eu)

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(15) R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

(16) E. Berliner, *J. Chem. Educ.*, **43**, 124 (1966).

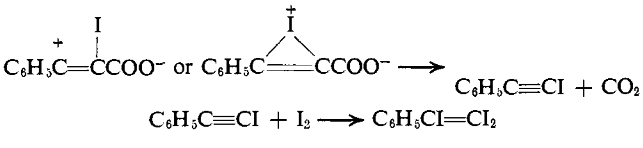
(17) D. S. Noyce, M. A. Matesich, and P. E. Peterson, *J. Amer. Chem. Soc.*, **89**, 6225 (1967).

(18) A referee has suggested the equilibria $A + {}_2I \rightleftarrows A\cdots I_2 \rightleftarrows AI^+ + I^-$ and rate-determining attack of water or iodide ion on the iodinated species as a kinetically alternate scheme to that expressed in eq 2.

also include contributions from all three terms, even though a good Arrhenius plot was obtained. For the first term, $E = 15.3$ kcal and $\Delta S^{\ddagger} - 23.5$ eu, but because of their composite nature, the activation parameters are not revealing as far as the mechanism is concerned.

Because the reaction of the free acid has the same dependence on iodide ion as the reaction of the anion, the same three mechanisms are likely to be involved also in its iodination.

The formation of triiodostyrene is not due to reaction of diiodocinnamic acid with iodine, followed by decarboxylation.[19] Sodium diiodocinnamate does not react with iodine to produce significant amounts of the styrene, even in 2 months. The most likely path for styrene formation is through the decarboxylation of a cationic intermediate followed by addition of iodine as shown



$$C_6H_5\overset{+}{C}{=}\overset{\overset{I}{|}}{C}COO^- \text{ or } C_6H_5C{=}CCOO^- \longrightarrow C_6H_5C{\equiv}CI + CO_2$$

$$C_6H_5C{\equiv}CI + I_2 \longrightarrow C_6H_5CI{=}CI_2$$

A similar situation has been found in the chlorination of cinnamic acid.[20] This would account for the observation that the lower the iodide ion concentration, the greater the amount of styrene, because iodide ion would intercept the intermediate. The small amount of triiodostyrene (1–3%) that is found in the iodine–iodide reaction is probably due to a small amount of reaction with free molecular iodine and phenylpropiolate anion.

It is not possible from our data to make definite statements about the nature of the intermediate and to decide if it is better represented by an open vinylic cation or a bridged unsaturated iodonium ion. The vinyl cation should have the positive charge next to the phenyl group and might lead to the formation of two β-keto acids (mono- and diiodinated). The bridged ion is more likely to be attacked at both carbon atoms. Since in isolation runs (except in those with no initial iodide ion) a minimum of three keto acids was formed, it is possible that the bridged ion is present in addition to the vinyl cation, or exclusively. Because the exact nature of the keto acids was not identified, further statements cannot be made.

Summary

The following conclusions may be drawn about the three reactions which were detected. (1) The reaction predominating at high iodide ion concentrations is a termolecular process involving iodine, iodide, and sodium phenylpropiolate. (2) The reaction whose rate is proportional to $1/(K_1 + I^-)$ is a reaction between iodine and sodium phenylpropiolate. (3) The reaction with a rate proportional to $1/(I^-)(K_1 + I^-)$ probably corresponds to iodination by the hydrated iodine cation. The total rate can therefore be represented by

$$-d(I_2)_t/dt = k_1(A)(I_2)(I^-) + k_2(A)(I_2) + k_3(A)(H_2OI^+)$$

The contribution of these reactions depends on the iodide ion concentration, the first one predominating at high, and the last at low iodide ion concentrations.

Experimental Section

Materials. Iodine and all salts were reagent grade chemicals. Phenylpropiolic acid (Aldrich Chemical Co.) was recrystallized from carbon tetrachloride, mp 136.5–137.3°. Its sodium salt was prepared by dissolving a slight excess of the acid contained in ethanol in an ethanolic solution of sodium ethoxide. Absolute ether was then added to dilute the ethanol. The white precipitate of sodium phenylpropiolate was filtered and washed twice with an absolute ether–ethanol mixture (95:5). The crude salt was refluxed with absolute ethanol for 20 min. If the pH of an aqueous solution of the salt was greater than 7, enough phenylpropiolic acid was added to the alcoholic solution to neutralize all traces of residual sodium ethoxide. The powdered salt was stored over phosphorus pentoxide. All samples were discarded after 1 month. α,β-Diiodocinnamic acid was prepared according to the literature and had mp 171.6–172.3° (lit.[10] mp 172°). Extensive discoloration and liberation of iodine occur at temperatures below the melting point. α,β,β-Triiodostyrene was prepared from silver phenylpropiolate and 2 equiv of iodine in benzene. Recrystallized from ethanol, it had mp 110.0–111.0° (lit.[21,22] mp 108, 112°). Benzoylacetic acid was prepared by hydrolysis of ethyl benzoylacetate in 2.5% potassium hydroxide. The crude product had mp 97.8–98.5° (lit.[23,24] 102–103°, 103–104°), neut equiv 166 (mol wt 164). Ethyl bromobenzoylacetate was produced by bromination of ethyl benzoylacetate, bp 132–138° (1 mm) (lit.[25] 135–137°), and contained some impurities by vpc. Alkaline hydrolysis of the bromo ester in 2.5 and 0.5% KOH yielded only benzoic acid, as did hydrolysis with 1 equiv of base. Acid hydrolysis in methanol–1 N sulfuric acid mixture did not proceed to a significant extent in 1 week. Several attempts to prepare iodobenzoylacetic acid from the bromo ester were not successful. Treatment of the bromo ester in ethanol with 1.1 equiv of NaI in acetone resulted in a brown oil, which on alkaline hydrolysis in 2.5% KOH afforded only benzoylacetic acid. Addition of 1 equiv of NaI to a 0.001 M solution of the bromo ester resulted in slow liberation of iodine. Addition of a trace of acid caused quantitative evolution of iodine. Slow iodine evolution was also observed in a neutral 40% aqueous methanolic solution of the bromo ester and NaI.

Kinetic Determinations. The temperature of the kinetic runs and the preparation of all stock solutions was 30°. For the determination of the activation parameters separate sets of solutions were made up at each temperature. Stock solutions of sodium phenylpropiolate (0.5 M) were always used within 2 days of preparation. Stock solutions of iodine were made up with various amounts of KI as required. All kinetic runs were carried out in glass-stoppered brown bottles. Reaction was started by adding 5 ml of an iodine–iodide solution to the reaction mixture. After vigorous shaking, a sample (5 or 10 ml) was withdrawn and run into 20 ml of 1 N sulfuric acid. This was taken as zero time. The iodine solution was titrated from a 5-ml buret graduated in hundredths with sodium thiosulfate solution of the same normality as that of the initial iodine concentration, except for the runs at a 0.0005 M concentration of iodine, for which 0.0020 M thiosulfate was used. Thiosulfate solutions were prepared by dilution of a 0.1 M stock solution and were discarded 10 hr after preparation. Reactions were conducted under second-order or pseudo-first-order conditions, and rate constants were calculated from the slopes of appropriate graphs. Duplicate runs agreed within ±2% and additional determinations were made if they did not. All rate constants in the tables, except those in Table I, are averages of duplicate runs. The two runs at zero initial iodide ion concentration gave poor second-order plots, probably because iodide ion was produced as a result of styrene formation. All of the low iodide runs exhibited a slight fall-off in rate constants after about 40% reaction. High-iodide runs showed no significant deviation from linearity up to about 70% reaction. Tests with blanks indicated no iodine loss from the reaction bottles during kinetic runs. All pH mea-

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[19] There is no evidence that the formation of triiodostyrene contributed to the rate constants. However, if some of the contribution attributed to the second term in eq 2 were due to the iodination of phenylacetylene, the deviation from linearity at high iodide ion concentration in Figure 5 might be explained.

[20] M. C. Cabaleiro, M. D. Johnson, B. E. Swedlund, and J. G. Williams, *J. Chem. Soc. B*, 1022 (1968).

[21] C. Liebermann and H. Sachse, *Chem. Ber.*, **24**, 4112 (1891).

[22] V. Franzen, *ibid.*, **87**, 1148 (1954).

[23] V. Leighton, *Amer. Chem. J.*, 20, 133 (1898).

[24] W. H. Perkin, *J. Chem. Soc.*, **45**, 170 (1884).

[25] B. Howk and S. McElvain, *J. Amer. Chem. Soc.*, **54**, 282 (1932).

surements were made with a Beckman Model G pH meter with 0.05 M acid phthalate as a standard.

Product Analysis. In all isolation runs initial concentrations of sodium phenylpropiolate and iodine were equal. Under these conditions reactions at high iodide ion concentrations did not go to completion, probably because equilibrium was reached, which is common in additions of iodine to multiple bonds.[4] Approach to equilibrium was not observed in kinetic runs because sodium phenylpropiolate was always in excess. Reactions at low iodide ion concentrations did go to completion, probably because of the irreversible formation of large amounts of triiodostyrene. For high iodide runs initial reactant concentrations were 0.050 or 0.025 M with iodide ion concentrations 0.80 or 0.40 M. Low iodide runs had initial reactant concentrations of 0.0005, 0.0008, or 0.001 M and initial iodide concentrations from zero to 0.001 M. In all runs, the triiodostyrene precipitate was collected by filtration and chloroform extraction of the walls of the container. The other products in the high iodide reaction were isolated by acidification followed by repeated chloroform extraction or by evaporation of the acidified solution to dryness under reduced pressure.

The low concentration of reactants of the low iodide runs made simple extraction inefficient. Evaporation of the acidified solution under reduced pressure resulted in low yields of the sensitive ketonic products. Lyophilization also resulted in low yields. The most satisfactory procedure was continuous extraction of the acidified mixture with ether for 48 hr followed by evaporation of the ether. Reagent grade absolute ether was required as other grades contained impurities which appeared to decompose the reaction products. With this procedure the percentage recovery of α,β-diiodocinnamic acid was 99%. The amount of materials recovered depended strongly on the conditions of evaporation of the ether. Three equal amounts of solution yielded 61, 78, and 94 mg of reaction product, the lowest yield corresponding to the most severe procedure and the highest yield to the lowest temperature in the work-up.

Product identification was made by thin layer chromatography and infrared spectra. Silica gel G (Merck) was used for all separations. For quantitative work with preparative plates, the silica gel was extracted with boiling ether before use. A mixture of 90% 30–40° ligroin–10% ether was found best for the separation of nonacidic substances. Acidic substances were separated best by chloroform saturated with 90% formic acid. A mixture of 88% 30–40° ligroin–12% acetic acid was also used for separation of acids; it gave poorer separation than the former but was useful when halogen tests were desired.

Visualization of spots was accomplished by exposure to iodine vapor or spraying with various reagents. All plates except those to be tested for halogen were first treated with iodine to visualize large spots. After the locations of these spots were marked, spray reagents were used if desired. A 0.4% solution of 2,4-dinitrophenylhydrazine in 2 N HCl was used to visualize most of the carbonyl compounds.[26] Enolic substances were detected with a mixture of 0.1 M ferric chloride and 0.1 M potassium ferricyanide.[26] No satisfactory spray reagent was found for halogen compounds. The least inconsistent results were obtained by spraying with a 0.5% ethanolic solution of silver nitrate followed by 10 min exposure to uv light.[27] All acids appeared to give weak tests which faded with time, but most halogen-containing compounds gave stronger spots, white on a brown background. All results with this reagent were considered tentative. The positive tests reported in the text were strong Beilstein tests on isolated materials.

Preparative plates were treated similarly. The appropriate band was then scraped off and extracted four or five times with boiling methanol. The filtered methanol solution was evaporated to dryness and the residue was extracted with ether, which was then evaporated. Tests with authentic samples of diiodocinnamic acid demonstrated that recovery from the plates averaged about 70%. Treatment of a low-iodide product mixture with Girard's reagent T separated the ketonic components from the other acids.[28] Extraction of a reaction mixture with bicarbonate and chromatography of the bicarbonate soluble fraction showed that at least 95% of the products, including all of the ketonic compounds, are acidic.

Of the three keto acids separated by chromatography one exists only in the enolic form; it gives a positive enol test but does not react with DNPH. The most abundant keto acid has a yellow DNPH derivative, while the least abundant has an orange one. These keto acids, mentioned in increasing mobility in chloroform–formic acid, were less mobile than the starting material, which was in turn less mobile than diiodocinnamic acid. In all calculations of yield it was assumed that production of one molecule of styrene required two molecules of iodine. Therefore, the amount of unreacted starting material at the completion of reaction was assumed equal to the per cent yield of styrene, because initial concentrations of iodine and sodium phenylpropiolate were equal. A solution 0.0016 M in sodium diiodocinnamate and 0.0008 M in iodine produced less than 1 mg of triiodostyrene in 2 months ($<0.5\%$).

Acknowledgment. This work was supported by National Science Foundation Grant GP-4986, which is gratefully acknowledged. We are also pleased to acknowledge a National Science Foundation Research Instrument Grant (GP-8271) for the purchase of a grating infrared spectrophotometer and a preparative gas chromatograph.

(26) J. Kirchner, "Technique of Organic Chemistry, Vol. XII. Thin Layer Chromatography," A. Weissberger, Ed., Interscience, New York, N. Y., 1967, pp 151–176.

(27) D. C. Abbott, H. Egan, and J. Thompson, *J. Chromatogr.*, **16**, 481 (1964).

(28) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, 1955, pp 88–89.