and 0.7 g (4 mmol) iodic acid in 50 mL of the standard solvent was heated at 65 °C for 5 h. The mixture was cooled and mixed with 100 mL of 1:1 petroleum ether–benzene. The whole was then washed with two 50-mL portions of water and one of 10% sodium thiosulfate. The solvent was removed by rotary evaporation, yielding 4.4 g of buff colored residue. Crystallization from hexane gave 2.8 g (68%) of light yellow colored 1,6-diiodo-2-methoxynaphthalene, mp 146–148 °C. Anal. Calcd for $C_{11}H_8OI$: C, 32.20; H, 1.95. Found: C, 32.24; H, 1.94. MS, *m/e* 410 (M^+, 100), 395 (M − 15, 22); ^1H NMR δ 7.17 (H-3, d, $J_{3,4}$ = 9.0 Hz), 7.68–7.71 (H-3 and H-7, m, 2 H, 8.10 (H-5, s), 7.86 (H-8, d, $J_{7,8}$ = 9.2 Hz); ^{13}C NMR δ 87.47 (C-1), 157.17 (C-2), 113.64 (C-3), 129.40 (C-4), 131.31 (C-4a), 136.64 (C-5), 89.34 (C-6), 136.45 (C-7, may be reversed with C-5), 133.07 (C-8), 134.76 (C-8a), 57.20 (methoxyl).

Ancillary Experiments. (a) The Reaction of 1-Iodo-2-methoxynaphthalene with Iodine. A mixture of 1-iodo-2-methoxynaphthalene (4.0 g, 15.7 mmol), 2.3 g (3.66 mmol) iodine, and 0.93 g (5.3 mmol) iodic acid were heated to 80 °C in 60 mL of the standard solvent. Aliquots (15 mL) were withdrawn after 1, 2, and 18 h. Each was poured into 50 mL of 10% sodium thiosulfate solution and filtered after 2 h. The collected solid residues were air-dried and analyzed by GC. The results were as follows: sample 1, starting material; sample 2, ca. 1:1 starting material and 1,6-diiodo-2-methoxynaphthalene; sample 3, 13% 2-methoxynaphthalene, 12% 6-iodo-2-methoxynaphthalene, 30% starting material, and 55% of the 1,6-diiodo-2-methoxynaphthalene.

(b) Reductions with HI. Samples of 1-iodo-2-methoxynaphthalene (0.284 g, 1 mmol) and the corresponding amount of the 6-iodo compound were placed in two test tubes respectively. Each was dissolved in 20 mL of the standard solvent, 2 g of potassium iodide was added, and the respective mixtures were heated to 80 °C for 1 h. These reactions were worked up as in a above. It was noted that the tube with the 1-iodo compound turned dark brown very rapidly, while the tube with the 6-iodo isomer darkened at a much slower rate. GC of the product from the former sample showed 98% 2-methoxynaphthalene and 2% starting material. The 6-iodo isomer appeared to be unreacted despite the color.

(c) Reaction with Iodic Acid. A solution of 3.60 g of 2-methoxynaphthalene in 60 mL of standard solvent was heated to 80 °C and 2.82 g (16 mmol) of iodic acid was added. The solution, which turned dark brown very rapidly, was heated for 18 h. It was then worked up as in a above. GC analysis indicated that it was equal parts of starting material and 1-iodo-2-methoxynaphthalene.

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Pathways in Chromic Acid Oxidations. 3.[1] Kinetics and Mechanism of Oxidation of Malonic Acid

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Pioneering and incisive studies by Westheimer, Wiberg, and Rocek have provided much of our understanding of the pathways in the chromic acid oxidation of organic substrates. The "chromate ester" mechanism of the oxidation of alcohols has been placed on firm grounds.[2,3] Rate-limiting C–H cleavage in the oxidation of 2-propanol[4] and diphenylmethane[5] is evident in the substantial primary kinetic isotope effect ($k_H/k_D \sim 6$). Chromium(VI) is also known to cleave C–C bonds in pinacol[6] and oxalic acid[7] with remarkable facility. In oxidations of cyclobutanol,[8] phenyl *tert*-butyl carbinol,[9] and mandelic acid,[10] where there is a possibility of either C–H and C–C cleavage, C–C cleavage products have been attributed to the highly reactive Cr(IV) and/or Cr(V) intermediates. The mechanism of C–C cleavage in oxalic acid has been investigated in detail. A definitive study has come from Rocek's group[7] in which the second-order term in oxalic acid was interpreted in terms of a one-step three-electron reduction of Cr(VI) to Cr(III). The oxidation of higher homologues have been reported,[11] where the site of oxidation is at the CH_2 rather than at the carboxyl.

Very little work has been done with malonic acid, in spite of the fact that this substrate is atypical in other oxidations. Only two reports[12,13] are available on the Cr(VI) oxidation of malonic acid, and they have been in narrow concentration ranges without any meaningful product analysis. We found that hydroxymalonic acid [HMA] is about 250 times more reactive than malonic acid, and it seemed very unlikely that it would accumulate in stoichiometric amounts. We wish to report in this paper a detailed kinetic and product study of the chromic acid oxidation of malonic acid.

$$3CH_2(COOH)_2 + 2Cr(VI) \rightarrow 3CH(OH)(COOH)_2 + 2Cr(III) \quad (1)$$

Experimental Section

Malonic acid (Aldrich, mp 136 °C) and hydroxymalonic acid (Sigma, mp 154 °C) were used without further purification. Deuteromalonic acid ($DOOCCD_2COOD$, Sigma, 99+ atom % D) was used as received. Sulfuric acid-d_2 (Sigma, D_2SO_4, 99.5+ atom % D, 98% solution in D_2O) was diluted in D_2O and was used for the determination of kinetic isotope effect. Sodium dichromate dihydrate (Baker analyzed) was used to prepare stock solutions of chromium(VI) and was standardized iodometrically and spectrophotometrically (a = 1560 M^{-1} cm^{-1} at 350 nm). $HClO_4$ (BDH, AnalaR, 70%) was further diluted in doubly distilled water to achieve the required hydrogen ion concentrations. Bromine (BDH; AnalaR) was used for the enolization studies.

Kinetics. (a) Oxidation of Malonic Acid. The kinetics of oxidation were followed under pseudo-first-order conditions, with at least a tenfold excess of malonic acid over chromium(VI), by monitoring the decrease in absorbance at 350 nm in a Cary-15 double-beam recording spectrophotometer, fitted with a thermostated cell holder. Kinetic measurements were carried out at 50 ± 0.2 °C, unless otherwise stated. Pseudo-first-order plots of the log of absorbance (350 nm) vs. time were linear through time courses greater than three half-lives, except for the first few initial points. Absorbance vs. time curves were closely similar to what

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Table I. Dependence on Cr(VI) in the Oxidation of Malonic Acid[a]

10^3 [Cr(VI)], M	10^3 [$HCrO_4^-$], M[b]	[malonic acid], M	10^5k_{obsd}, s^{-1}	10^5k_2, M^{-1} s^{-1}
1.12	0.96	0.44	19.3	43.9
1.88	1.50	0.5	21.4	42.8
4.35	2.9	0.5	21.1	42.2
8.84	4.9	0.5	20.6	41.2

[a] [$HClO_4$] = 0.5 M; 50 °C. [b] [$HCrO_4^-$] = $[(1 + 8K_d[\mathrm{Cr(VI)}])^{1/2} - 1]/4K_d$ where $K_d = [Cr_2O_7^{2-}]/[HCrO_4^-]^2$ = 80.5 M^{-1} at 0.5[H$^+$].

has been observed by Rocek in the chromic acid oxidation of oxalic acid[7] and glycolic acid.[14] The slope of the linear parts of the plots were used to determine the values of the observed pseudo-first-order rate constants. Rate constants were reproducible to ±5% in duplicate measurements.

(b) Rate of Enolization of Malonic Acid. Enolization rates for malonic acid were measured by the traditional bromination method. Bromine (AnalaR) was dissolved in aqueous perchloric acid solutions, and the initial concentration of bromine was determined iodometrically and by measuring the absorbance at 393 nm (a = 164 M^{-1} cm^{-1}).[15] The iodometric method for monitoring the bromination of malonic acid failed because the product monobromomalonic acid also oxidizes iodide ions to iodine. Zero-order bromination rates could be measured spectrophotometrically by monitoring the linear decrease in absorbance due to bromine at 393 nm. The loss of bromine was near instantaneous at 50 °C, the temperature at which most of the chromic acid oxidation rates have been measured. Enolization studies were therefore performed at 25 °C. The rates of enolization were calculated from the relation[16] in eq 2, using a 1-cm cell, where k_o is the slope of the

$$k_{en} = \frac{k_o}{[\mathrm{M}]_T a_{Br}^{393}} \tag{2}$$

linear plot of A_{393} vs. time, $[\mathrm{M}]_T$ is the total analytical concentration of malonic acid, and a_{Br} is the molar absorptivity of bromine at 393 nm (164 M^{-1} cm^{-1}). The equilibrium concentration of the enol has been estimated to be less than 0.01% by Haim and Leopold[16] from stopped-flow spectrophotometric measurements. The concentration of bromine was kept in the range (1–2) × 10^{-3} M so that the bromination reaction is zero order with respect to bromine.

Product Analysis. In a typical experiment malonic acid [1 M], H$^+$ [0.5 M], and Cr(VI) [0.02 M] in a total volume of 100 mL were left for 10 h (>10 half-lives) at 50 °C.

Estimation of Hydroxymalonic Acid. One milliliter of a 1:10 dilution of 85% H_3PO_4, 1.6 mL of 10 N H_2SO_4, 1 mL of 2.5% ammonium molybdate solution, and 1 mL of the reaction mixture were mixed in the oder indicated. The reaction mixture was made up to 10 mL and was heated on a water bath for 15 min. The absorbance of the resulting blue solution[17] was measured at 760 nm. A calibration curve was obtained with known concentrations of HMA. A control experiment was run with malonic acid alone, and this did not interfere with the measurement.

Estimation of Glyoxylic Acid. Fifty milliliters of the reaction mixture was treated with 200 mL of a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl and was left overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone was filtered, dried and weighed (mp 194 °C). The filtrate was continuously extracted with ether. The ether extract was dried [$MgSO_4$] and evaporated. The residue was extracted with a saturated solution of bicarbonate, leaving behind the unreacted 2,4-dinitrophenylhydrazine which was rejected. The bicarbonate extract was acidified, reextracted with ether, dried, and evaporated to leave an additional amount of 2,4-dinitrophenylhydrazone of glyoxylic acid. A solution of this derivative in MeOH–KOH showed λ_{max} at 420 nm[18] (a = 4.02 × 10^4 M^{-1} cm^{-1}), and this was identical with that of an authentic sample.

Results and Discussion

Cr(VI) Dependence. Pseudo-first-order rate constants (k_{obsd} s^{-1}) have been calculated from the linear parts of the plots of log A_{350} vs. time. Rate constants for various initial concentrations of Cr(VI) are given in Table I. It is observed that for a eightfold variation in total Cr(VI) and fivefold change in the $HCrO_4^-$ concentration[19] the pseudo-first-order rate constant is essentially constant, indicating that the oxidation reaction is first order in total Cr(VI). Chromic acid oxidations proceeding through the ester mechanism have been shown to have a first-order dependence on $HCrO_4^-$ rather than on the total Cr(VI).[2,3] Wiberg had observed a dependence on total Cr(VI) in the oxidation of diphenylmethane.[5] In cyclopropanol oxidations[20] the oxidation rate was found to be first order in total Cr(VI) in spite of the fact that oxidation is routed through the chromate ester. The reason for this differential dependence is not clear.

Substrate Dependence. Oxidation rates were measured in a wide range of malonic acid concentrations at several hydrogen ion concentrations. The rate constants are given in Table II. At lower acidities the first-order dependence on malonic acid is clearly evident, and this is seen in the nearly constant values of the second-order rate constant. At higher acidities (0.95–2.5 M, $HClO_4$), the second-order rate constants drifted, and higher values of k_2 at lower malonic acid concentrations were obtained. Two possible reasons can be advanced to explain this situation. (1) A kinetically detectable complex between malonic acid and chromic acid could lead to the observed substrate dependence. Correlation coefficients for the double reciprocal plots of $1/k_{obsd}$ vs. 1/[malonic acid] were poor, except for the data at [H$^+$] = 2.5 M. The value of K_{eq} at this acidity was estimated to be 1.1. Values of K_{eq} roughly estimated were internally inconsistent. No real trend toward saturation could be established. (2) The second-order rate constants were nearly constant at higher malonic acid concentrations at all the acidities. This leads us to believe that the unusual departure from the strict first-order dependence on malonic acid is not a consequence of complex formation. This may well be an artifact, due to incursion of a faster oxidation of a product formed in the oxidation and this should be particularly reflected at lower values of [MA]/[Cr(VI)] and at higher acidities. Oxidation rates for a number of likely intermediates were measured and it was found that the intermediates are reacting 180 to 700 times faster than malonic acid (Table VI).

Acidity Dependence. A straightforward first-order dependence on [H$^+$] in the range 0.1–0.5 M $HClO_4$ was observed. Rate constants were corrected to give allowance for the equilibrium in eq 3. A value of 4.0 M for K_a[21] was

$$H_2CrO_4 \overset{K_a}{\rightleftharpoons} HCrO_4^- + H^+ \tag{3}$$

used. For acidities ≥ 0.95 M $HClO_4$, h_0[22] values were used. Third-order rate constants (last column in Table II) showed a less than first-order dependence on [h_0] at higher acidities.

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Table II. Substrate Dependence in the Chromic Acid Oxidation of Malonic Acid[a]

$[H^+]$, M	[malonic acid], M	10^5k_{obsd}, s^{-1}	10^5k_2, M^{-1} s^{-1}	$10^5k_2'$[b], M^{-1} s^{-1}	$10^5k_2'/[H^+]$, M^{-2} s^{-1}
0.095	0.05	0.44	8.8	9.01	94.8
	0.1	0.89	8.9	9.10	95.7
	0.5	3.46	6.9	7.06	74.3
	0.75	5.23	6.97	7.13	75.0
	1.0	7.76	7.76	7.94	83.6
0.5	0.02	0.97	48.5	52.9	106
	0.05	2.35	47.0	52.9	106
	0.1	4.38	43.8	49.3	98.5
	0.2	9.13	45.6	51.3	102
	0.44	19.3	43.8	49.3	98.5
	0.5	20.1	40.2	45.2	90.4
	1.0	42.3	42.3	47.6	95.2
0.95	0.05	7.52	150	200	148
(h_o = 1.35)[c]	0.1	12.4	124	166	123
	0.25	22.0	88	117	87.1
	0.5	40.1	80.2	107	79.4
	0.75	50.9	68.0	90.9	67.3
	1.0	67.0	67.0	89.6	66.3
1.45	0.02	4.8	240	438	133
(h_o = 3.3)	0.1	17.6	176	321	97.3
	0.5	60.0	120	219	66.3
	0.75	71.5	95.3	174	52.7
	1.0	91.3	91.3	166	50.5
1.86	0.02	11.0	550	1237	247
(h_o = 5.0)	0.1	25.2	252	567	113
	0.2	45.4	227	511	102
	0.5	109	218	490	98.1
	1.0	185	185	416	83.2
	2.0	295	147	331	66.4
2.5	0.05	26.0	520	1827	181
(h_o = 10.06)	0.10	48.3	483	1697	169
	0.2	91.0	455	1599	159
	0.5	174	348	1223	121
	0.75	227	302	1061	105
	1.0	282	282	991	98.5

[a] $[Cr(VI)] = 6 \times 10^{-4}$ M; 50 °C. [b] $k_2' = k_2 (K_a + H^+)/K_a$ where K_a is the equilibrium constant for the reaction. $H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$. A value of 4.0 was used.[21] [c] Values of h_o have been taken from ref 22.

Table III. Malonic Acid Oxidation Data

a. Oxidation Rates for Malonic Acid-d_4[a]

$[H^+]$, M	10^5k_{2D}, M^{-1} s^{-1}	10^5k_{2H}, M^{-1} s^{-1}	k_H/k_D
0.05	3.7	4.4	1.2
0.1	6.5	8.9	1.36
0.5	34.2	43.8	1.28
0.95	101[b]	124[b]	1.2

b. Deuterium Kinetic Isotope effect in the Oxidation of Malonic Acid-d_4[c]

$[D_2SO_4]$, M	[malonic acid-d_4], M	k_D, s^{-1}	k_H[d], s^{-1}	k_H/k_D
3.6	0.5	5.4×10^{-4}	1.36×10^{-3}	2.5
1.8	0.5	3.94×10^{-4}	9.5×10^{-4}	2.4

[a] 50 °C; $[Cr(VI)] = 1 \times 10^{-3}$ M, [malonic acid] = 0.5 M. [b] [Malonic acid] = 0.1 M. [c] In D_2SO_4–D_2O. [d] In H_2SO_4–H_2O, using protiomalonic acid.

Table IV. Temperature Dependence in the Chromic Acid Oxidation of Malonic Acid[a]

T, °C	[malonic acid], M	10^5k_{obsd}, s^{-1}	10^5k_2, M^{-1} s^{-1}	E_a, kcal/mol	$\Delta S^‡$, eu[b]
30	0.5	4.24	8.48		
40	0.5	8.85	17.7	14.6	−36.3
50	0.44	19.3	43.8		
60	0.5	40.4	80.8		
70	0.5	68.2	136		

[a] $[H^+] = 0.5$ M, $[Cr(VI)] = 1 \times 10^{-3}$ M. [b] $\Delta S^‡/4.576 = \log k - 10.753 - \log T + E_a/4.576T$, calculated at 50 °C.

Oxidation of Deuteromalonic Acid. Oxidation rates for deuteromalonic acid were measured in the acidity range 0.05–1.0 M $HClO_4$, in aqueous medium. The rate data are given in Table III,a. A small value of k_H/k_D was observed. ^{1}H NMR indicated a rapid exchange of the deuterium with the solvent. Oxidation rates for deuteromalonic acid were therefore measured in D_2SO_4–D_2O. The k_H/k_D value of 2.5 (Table III,b) indicated a secondary isotope effect. Rate-limiting C–H cleavage in chromic acid oxidations are known for the high values of k_H/k_D (~6–8).[2,3] It was of interest to see if the oxidation reaction had a solvent isotope effect. k_{D_2O}/k_{H_2O} was found to be 1.2 ([malonic acid] = 0.5 M, $[HClO_4]$ = 0.5 M). The increase in rate in D_2O seems to be a marginal effect, when compared to the solvent isotope effect of 2.4 (k_{D_2O}/k_{H_2O}), observed for the chromic acid oxidation of alcohols.[2] The solvent isotope effect in alcohol oxidation can be considered as "pure", due to the fact that the CH hydrogen is inert to exchange in D_2O. In malonic acid oxidation the acidity of the methylene hydrogens results in a situation in which the solvent isotope effect is mixed up with the effect of deuterium substitution.

Temperature Dependence and Activation Parameters. Oxidation rates were measured at five temperatures in the range 30–70 °C, and the activation parameters were calculated from the linear plot of log k vs. T^{-1} (Table IV). The E_a value of 14.6 kcal/mol is 13 kcal lower than the reported value[13] of 27.6 kcal/mol.

Oxidation Products. Hydroxymalonic acid and glyoxylic acid were the two products that could be quantitated by standard methods (Table V). Unfortunately we have not been able to detect and quantitate other possible oxidation products derived from intermediates like HMA and GA in the presence of a large excess of malonic

Table V. Reaction Products in the Oxidation of Malonic Acid

			mol of product/mol of Cr(VI)		
$[H^+]$, M	[malonic acid], M	[Cr(VI)], M[a]	HMA	GA[b]	total[c]
0.5	1.0	0.02	0.2	0.3	0.8

[a] [Cr(VI)] = 0.02 M in 100 mL. [b] Glyoxylic acid (GA) is a four-electron oxidation product. Hence in the calculation of material balance the yield of GA is multiplied by a factor of 2. [c] The total theoretical yield = 1.5.

acid. The likely intermediates are oxalic acid, ketomalonic acid, and formaldehyde. The oxidation rates for the intermediates are given in Table VI.

Mechanism. Any mechanism for the chromic acid oxidation of malonic acid should take into account the following features: (1) The rate law for the oxidation (eq 4) is valid over a wide range of malonic acid concentrations

$$\frac{-\mathrm{d}[\mathrm{Cr(VI)}]}{\mathrm{d}t} = k[\text{malonic acid}][\mathrm{H}^+][\mathrm{Cr(VI)}] \qquad (4)$$

at lower acidities. (2) Hydroxymalonic acid and glyoxylic acid are the two major products formed in considerable amounts. (3) Glyoxylic acid is a product of oxidation of hydroxymalonic acid. (4) The k_H/k_D value of 2.5 in D_2SO_4–D_2O is a secondary isotope effect.

The absence of a primary deuterium kinetic isotope effect rules out rate-limiting C–H cleavage. One could conceive of an alternate route to hydroxylation through the reaction of an enol intermediate. The observed first-order dependence on chromium(VI) points to the fact that the intermediate (if any) reacts with chromium(VI) in a slow oxidation step. The enolization of malonic acid should be faster than its oxidation by chromium(VI) for the enol to be a reactive intermediate.

The enolization of malonic acid was first studied by West.[23] This has been in addressed in part, in studies of chemical oscillations by Noyes[24] and co-workers and by Beck,[25] involving bromate–malonic acid–cerium(IV) system. Haim and Leopold[16] studied the enolization of malonic acid and established a rate law (eq 5) at 25 °C.

$$k_{\mathrm{en}} = (2 \times 10^{-3}) + (1 \times 10^{-2})[\text{malonic acid}] \qquad (5)$$

The enolization rate of 2.3×10^{-3} s^{-1} due to Haim[16] was comparable to the value of 6×10^{-3} s^{-1} obtained by Beck[25] under identical conditions of acidity ($[H^+] = (1.88 - 7.51) \times 10^{-2}$ M). The enolization rate was found to be insensitive to hydrogen ions below pH 2. Field, Körös, and Noyes reported a rate law for the enolization, which has a first-order term in $[H^+]$ (eq 6). Enolization rates for malonic

$$k_{\mathrm{en}} = (1.3 \times 10^{-2})[\mathrm{H}^+][\text{malonic acid}] \qquad (6)$$

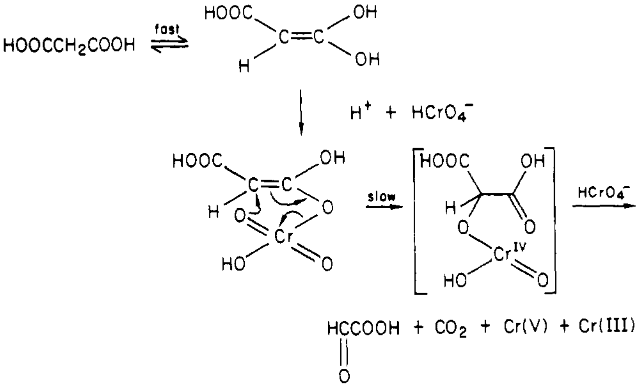
acid were measured by the bromination method. At $[H^+] = 0.1$ M and 25 °C, k_{en} was found to be $(5 \pm 0.4) \times 10^{-3}$ s^{-1}. This value is 100 times faster than the first-order oxidation rates for malonic acid at 50 °C. Clearly the enolization is extremely fast compared to the chromic acid oxidation rates. Enolization rates at $[H^+] = 0.5$ M were too fast to be accurately measured even at 25 °C. The enolization studies support the idea that the rapidly formed enol is undergoing a slow oxidation with chromic acid.

Table VI. Oxidation Rates for Malonic Acid and Some Likely Intermediates[a]

substrate	$10^5 k_{obsd}$, s^{-1}
malonic acid	0.29
hydroxymalonic acid	82.2
oxalic acid	207.0
formaldehyde	54.0
ketomalonic acid	b

[a] $[H^+] = 0.1$ M; [substrate] = 0.1 M, [Cr(VI)] = 1×10^{-3} M; 35 °C. [b] Very fast.

Scheme I



A most probable reaction sequence is given in Scheme I. The initial rate-limiting step involves a two-electron oxidation to hydroxymalonic acid. In this scheme it is suggested that the chromium(IV) intermediate, presumably bound to hydroxymalonic acid, is oxidized by another molecule of chromic acid to glyoxylic acid, CO_2, chromium(V), and chromium(III). Alternatively, the chromium(IV) intermediate may act directly as an one-electron oxidant. Reactions in eq 7–9 give a good accounting of the products formed in this oxidation.

$$\mathrm{CHOH(COOH)_2 + Cr(IV) \rightarrow {\cdot}COOH + OHCCOOH + Cr(III)} \qquad (7)$$

$$\mathrm{{\cdot}COOH + Cr(VI) \rightarrow CO_2 + Cr(V)} \qquad (8)$$

$$\mathrm{CH_2(COOH)_2 + Cr(V) \rightarrow CHOH(COOH)_2 + Cr(III)} \qquad (9)$$

Further evidence for a reactive enol intermediate comes from preliminary observations[26] that methylmalonic acid is oxidized essentially at the same rate as that of malonic acid and that dimethylmalonic acid is extremely unreactive.

It is clear from the data in Table VI that HMA is about 250 times more reactive than malonic acid. This reactivity difference is evident only for the Cr(VI) step. It could be even higher for a Cr(IV) intermediate. Oxidation rates in the presence of acrylamide were essentially unaffected, and thus the involvement of the radicals could not be directly demonstrated. Oxidation rates were also unaffected when conducted in a nitrogen atmosphere excluding oxygen. This study shows that there is very little direct C–C cleavage of malonic acid (eq 10). Even though glyoxylic

$$\mathrm{HOOCCH_2COOH + Cr(VI) \rightarrow HOCH_2COOH + Cr(IV) + CO_2} \qquad (10)$$

acid could conceivably be produced by the oxidation of glycolic acid, the formation of HMA in significant amounts

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rules out this reaction as a major pathway for malonic acid oxidation. Our scheme assumes that the first mole of HMA is oxidized to GA and that an additional mole of HMA is obtained in the Cr(V) step. Clearly some oxidation of GA has also occurred.

It is relevant to compare the Cr(VI) oxidation of malonic acid with other oxidizing agents. The formation of the radical $\cdot CH(COOH)_2$ has been suggested in oxidations by one-electron oxidizing agents[27] like V(V) and Mn(III) pyrophosphate. The postulation of this radical and the reported second-order dependence on V(V) and Mn(III) are in direct conflict. The involvement of the malonic acid radical has been demonstrated in the Ce(IV) oxidation by flow ESR techniques.[28,29] What makes the Ce(IV) oxidation so unique to be different from V(V), Mn(III), and Cr(VI) oxidations is not clear at this moment.

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Registry No. Malonic acid, 141-82-2; hydroxymalonic acid, 80-69-3; glyoxylic acid, 298-12-4; 2,4-dinitrophenylhydrazine, 119-26-6; glyoxylic acid 2,4-dinitrophenylhydrazone, 3158-42-7; oxalic acid, 144-62-7; formaldehyde, 50-00-0; ketomalonic, 473-90-5.

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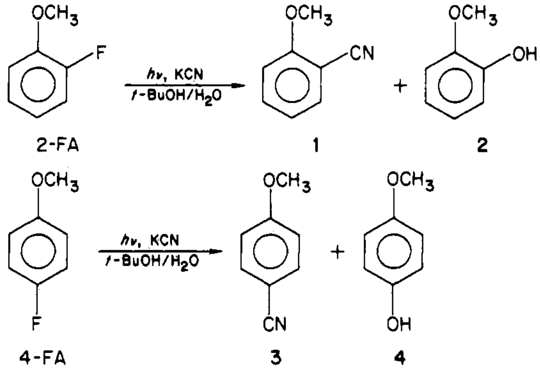
Communications

Anomalous Effects during Aromatic Nucleophilic Photosubstitutions of 2- and 4-Fluoroanisoles in Solvent Mixtures of Water and *tert*-Butyl Alcohol

Summary: The rate constant ratio for removal of fluorine by either cyano or hydroxy during aromatic nucleophilic photosubstitutions on 2- or 4-fluoroanisole displays a remarkable dependence upon the composition of the water/*tert*-butyl alcohol solvent and the distance between the methoxy group and the site of substitution in the solutes.

Sir: Our recently completed studies[1] indicated that the efficiency and selectivity of aromatic nucleophilic photosubstitutions (by water and cyanide) on 2- or 4-fluoroanisole (2- or 4-FA) are influenced in several different ways by addition of cyclodextrin, a torus-shaped polyalcohol, to an aqueous solvent. In order to separate some of these effects, we have examined the substitution reactions when *tert*-butyl alcohol replaces the cyclodextrin.

Nucleophilic strengths of cyanide and water in aqueous solvent mixtures usually fall between those measured in each of the neat solvent components[2] and are relatively insensitive to reactive substrates within the same class.[3,4] The Hughes–Ingold theory,[5] Swain–Scott equation,[6] and others which relate solvent bulk properties and rates of substitution reactions[6b,7] predict a monotonous decrease in the nucleophilicity of cyanide with respect to water (including hydroxide) as an aqueous solvent is enriched in a less polar cosolvent like an alcohol. We find that the selectivity of aromatic nucleophilic photosubstitutions on 2-FA or 4-FA in aqueous *tert*-butyl alcohol[8] is totally inconsistent with these relationships and varies in opposing ways with the FA isomer.



The mechanism of aromatic nucleophilic photosubstitution reactions of FA in aqueous *tert*-butyl alcohol has been reviewed recently[9] and Varma and co-workers[10] have

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[8] (a) Traces of an oxidation product, 4-cyano-2-fluoroanisole, from 2-FA were detected. Small amounts of another unidentified photoproduct were obtained from 4-FA. No formation of anisole[8b] or *tert*-butoxyanisole was detected from either FA isomer. All products were identified by comparisons with authentic samples. They account for more than 85% of consumed FA. Product ratios were determined on the unadulterated reaction mixtures by HPLC and are corrected for differing UV detector responses. All experiments were conducted with 2×10^{-3} M FA and 0.1 M KCN in nitrogen-saturated solutions at room temperature. Irradiations at 254 nm for 2-FA and >260 nm for 4-FA were kept below 10% conversion for most runs and never reached 20%. A more detailed description of experimental procedures is included in ref 1. (b) Houser, J. J.; Siegman, J. R. *J. Org. Chem.* **1982**, *47*, 2773.

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