Kinetics and Mechanism of the Oxidation of Substituted Malonic Acids by the Hexachloroiridate(IV) Ion

Giuseppe Calvaruso, Antonio I. Carbone, and F. Paolo Cavasino *
Istituto di Chimica Fisica, Università, 90123 Palermo, Italy

The kinetics of oxidation of malonic acid (H_2mal) and its n-butyl (H_2bmal), benzyl (H_2bzmal), and phenyl (H_2pmal) derivatives by hexachloroiridate(IV) ion have been studied at ionic strength 0.50 mol dm^{-3} and at various temperatures, over a wide acidity range. The reactions are first order with respect to the concentrations of the oxidant and the reducing agents. The rates are enhanced by a decrease in the hydrogen-ion concentration, and are sensitive to the substituent group, increasing in the order $H_2mal < H_2bmal < H_2bzmal < H_2pmal$. A reaction mechanism is proposed and discussed. The first dissociation constant of the dicarboxylic acids and the corresponding thermodynamic parameters have also been obtained kinetically.

The kinetics and the mechanism of oxidation of malonic acid have been widely investigated[1,2] by using a variety of oxidizing agents under different experimental conditions. However, as far as we know, no detailed kinetic study on the oxidation of this substrate by hexachloroiridate(IV) anion has been carried out. Indeed relatively few investigations on the kinetics of iridium(IV) oxidation of organic compounds have been reported,[3—7] even though the use of this oxidant is convenient because of its stability towards substitution or hydrolysis over a wide range of acidity.

According to some previous measurements of reactivity, malonic acid was found[4] to be fairly resistant to Ir^{IV}, but its monoanion was more easily oxidized. Moreover, additional measurements performed in our laboratory using mono- and di-substituted malonic acids showed that the reactivity of Ir^{IV} towards these organic compounds was strongly dependent on the substituent group(s) present in the malonic acid. Therefore it was of interest to investigate in detail the kinetics of oxidation of some malonic acid derivatives by the hexachloroiridate(IV) ion in order to obtain information about the reaction mechanism and the substituent effects on the oxidation rate. The kinetics were studied over a wide acidity range at ionic strength 0.50 mol dm^{-3} and at three temperatures to estimate the activation parameters. The organic substrates examined were malonic acid (H_2mal) and its n-butyl (H_2bmal), benzyl (H_2bzmal), and phenyl (H_2pmal) derivatives. The stopped-flow method was used to follow the fastest oxidations involving the phenyl derivative, whereas a conventional spectrophotometric technique was employed for the remaining reactions. Under similar experimental conditions, dimethylmalonic and di-n-propylmalonic acids were found to be unreactive. The first dissociation constant (K_1) of the dicarboxylic acids considered and the corresponding thermodynamic parameters have also been estimated kinetically.

Experimental

Materials.—The dicarboxylic acids were prepared and purified as described elsewhere.[8] Merck reagent-grade sodium hexachloroiridate(IV) was utilized to prepare acidic stock solutions of this salt, which were used within a few hours of preparation. They were standardized spectrophotometrically[6,7,9] at 488 nm using ε = 4 050 dm^3 mol^{-1} cm^{-1}. Potassium hexachloroiridate(III) and acrylamide were supplied by Alfa and Fluka, respectively. Standard solutions of these substances and of the dicarboxylic acids were prepared by weight. Very pure Fluka sodium perchlorate and perchloric acid were used to adjust the solutions to the desired ionic strength (= 0.50 mol dm^{-3}) and acidity. The hydrogen-ion concentrations were determined from pH-meter readings by use of a calibration curve. All the solutions were prepared using deionized water purified by distillation from an alkaline permanganate solution.

Kinetics.—The kinetic measurements were performed at various acidities and temperatures under conditions of an excess of the reducing agent and monitored spectrophotometrically by following the rate of disappearance of Ir^{IV} at 460—500 nm, where Beer's law was found to be obeyed. The measurements were made with a Beckman DU or a Beckman DK-2A recording spectrophotometer equipped with thermostatted cell compartments. For the fastest reactions involving phenylmalonic acid a Durrum-Gibson stopped-flow spectrophotometer (D-130) was used. In most experiments the disappearance of Ir^{IV} followed a first-order rate law for at least four half-lives, but at the highest acidities and lowest [reductant]/[Ir^{IV}] ratios examined departures from this law were observed after 60—70% reduction of Ir^{IV}. The estimated pseudo-first-order rate constants, $k_{obs.}$, were reproducible within ±3%. Some kinetic runs were carried out in the presence of hexachloroiridate(III) ions at concentrations of up to four times the initial concentration of Ir^{IV}. Polymerization tests were also made in some cases in the presence of 20% (w/v) of acrylamide and a decrease in the rates of 10—20% was observed.

Stoicheiometry.—The reaction stoicheiometry was determined by allowing a solution containing Ir^{IV} and reductant in the molar ratio 10:1 to react until the iridium(IV) concentration had reached a steady value. The unreacted oxidant was estimated spectrophotometrically at 488 nm. For each reducing agent examined, two experiments, using different quantities of the reactants and hydrogen ion, showed that 4.1 ± 0.1 mol of Ir^{IV} reacted per mol of organic substrate.

Under conditions of equal molar concentrations of Ir^{IV} and the reducing agents, the reaction mixtures, after extraction with diethyl ether, gave positive tests with 2,4-dinitrophenylhydrazine, establishing the presence of a carbonyl group in the oxidation product. In the case of phenylmalonic acid the precipitated hydrazone was separated and its m.p. determined. The value found (195 °C) corresponded[10] to that (196—197 °C) of the hydrazone of $C_6H_5COCO_2H$. These findings are consistent with the estimated reaction stoicheiometry.

Table 1. Dependence of the pseudo-first-order rate constants on the reductant concentration (ionic strength = 0.50 mol dm^{-3}, [Ir^{IV}] = 2.00 × 10^{-4} mol dm^{-3}, 25.0 °C)

$10^3[H^+]$	$10^2[H_2A]_T$	$10^3k_{obs.}[H_2A]_T^{-1}$/
mol dm^{-3}		dm^3 mol^{-1} s^{-1}
(*a*) Malonic acid[a]		
8.11	0.500	6.82
8.11	1.00	6.90
8.11	1.50	6.80
8.11	2.00	6.50
8.11	5.00	6.80
15.8	0.500	3.92
15.8	1.00	3.81
15.8	1.50	3.68
15.8	2.00	4.10
15.8	5.00	3.82
(*b*) n-Butylmalonic acid		
3.51	0.500	19.6
3.51	0.750	20.7
3.51	1.00	20.7
3.51	3.00	19.0
3.51	5.00	19.6
10.1	0.500	8.80
10.1	0.750	8.55
10.1	1.00	8.42
10.1	3.00	8.77
10.1	5.00	8.40
(*c*) Benzylmalonic acid		
7.60	0.500	56.0
7.60	0.750	56.3
7.60	1.00	57.2
7.60	2.00	56.0
7.60	3.00	57.0
7.60	5.00	55.6
30.2	0.500	16.5
30.2	0.750	16.3
30.2	1.00	16.8
30.2	2.00	17.1
30.2	3.00	16.7
30.2	5.00	17.1
(*d*) Phenylmalonic acid[b]		
14.9	1.00	374
14.9	2.00	325
14.9	5.00	364
14.9	7.00	371
14.9	10.0	334

[a] At 45.0 °C. [b] [Ir^{IV}] = 1.08 × 10^{-4} mol dm^{-3}.

Results and Discussion

At a given temperature and at constant hydrogen-ion and total organic substrate concentrations, the observed pseudo-first-order rate constants, $k_{obs.}$, are independent of the initial iridium(IV) concentration used (1.0 × 10^{-4}—6.0 × 10^{-4} mol dm^{-3}), indicating that the reactions are first order with respect to this reagent. Addition of $IrCl_6^{3-}$ to the solutions has no effect on the reaction rate, suggesting that the rate-determining step is not preceded by an equilibrium involving Ir^{III}. At constant temperature and acidity the rate constants $k_{obs.}$ depend on the total concentration of the reductant, $[H_2A]_T$. Dividing the $k_{obs.}$ values by $[H_2A]_T$, nearly constant values for the second-order rate constants (k_2) are obtained (see Table 1). Moreover plots of $k_{obs.}$ against $[H_2A]_T$ yield straight lines with zero intercepts. Therefore, the redox reactions investigated are also first order with respect to the reductants and, under the experimental conditions used, formation of intermediate complexes is not indicated by the kinetic data, in accordance with an outer-sphere electron-transfer process as usually observed for iridium(IV) oxidations.

According to these findings the rate of disappearance of Ir^{IV} is given by equation (1), where $k_2 = k_{obs.}/[H_2A]_T$.

$$-d[Ir^{IV}]/dt = k_{obs.}[Ir^{IV}] = k_2[H_2A]_T[Ir^{IV}] \qquad (1)$$

The oxidation rates were found to be sensitive to the acidity of the medium. For each reducing substrate examined the acid dependence of the rate was studied at three temperatures at fixed $[H_2A]_T$ and [Ir^{IV}] by varying the perchloric acid concentration, the ionic strength being held constant at 0.50 mol dm^{-3}. Figures 1—4 show that in each case investigated a plot of $1/k_2$ against [H$^+$] yields a straight line with positive intercept in accordance with equation (2), where the constants k_a and k_b

$$1/k_2 = k_a + k_b[H^+] \qquad (2)$$

depend on both the temperature and the substrate used. The values of these constants, as estimated by a weighted least-squares method, are listed in Table 2.

The present kinetic data can be reasonably interpreted with the reaction mechanism in equations (3)—(5) [H_2A = $RCH(CO_2H)_2$ with R = H, n-C_4H_9, $C_6H_5CH_2$, or C_6H_5; radical = $^{\bullet}CR(CO_2H)(CO_2^-)$]. According to this reaction

$$H_2A \overset{K_1}{\rightleftharpoons} H^+ + HA^- \qquad (3)$$

$$Ir^{IV} + HA^- \xrightarrow[\text{slow}]{k} \text{Radical} + H^+ + Ir^{III} \qquad (4)$$

$$\text{Radical} \xrightarrow[\text{fast}]{+Ir^{IV}} \text{Products} \qquad (5)$$

scheme, the rate-determining step is the outer-sphere electron-transfer process (4) involving Ir^{IV} and the monoanion of the reductant, an intermediate free radical being formed. The formation of the free radical is consistent with the reduced rate observed in the presence of acrylamide (*cf.* Experimental section) and has also been suggested previously[1] in the oxidation of malonic acid by different oxidants. Free-radical formation has also been proposed[3,4,7] in the iridium(IV) oxidation of various organic substrates. Moreover the step (4) would be in accordance with the fact that the dimethyl and di-n-propyl derivatives of malonic acid are unreactive (*cf.* Introduction). Reaction (5) would include more than one stage.

If the assumption is made that the estimated reaction stoicheiometry is valid under the conditions of the kinetic experiments (*i.e.* in the presence of an excess of reducing agent),

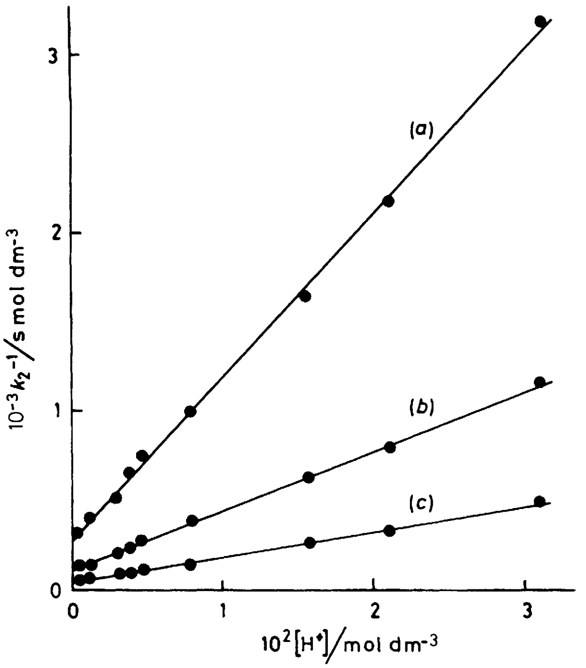

Figure 1. Plot of $1/k_2$ against $[H^+]$ for malonic acid at 25.0 (*a*), 35.0 (*b*), and 45.0 °C (*c*); $[Ir^{IV}] = 2.00 \times 10^{-4}$, $[H_2A]_T = 1.00 \times 10^{-2}$ mol dm^{-3}

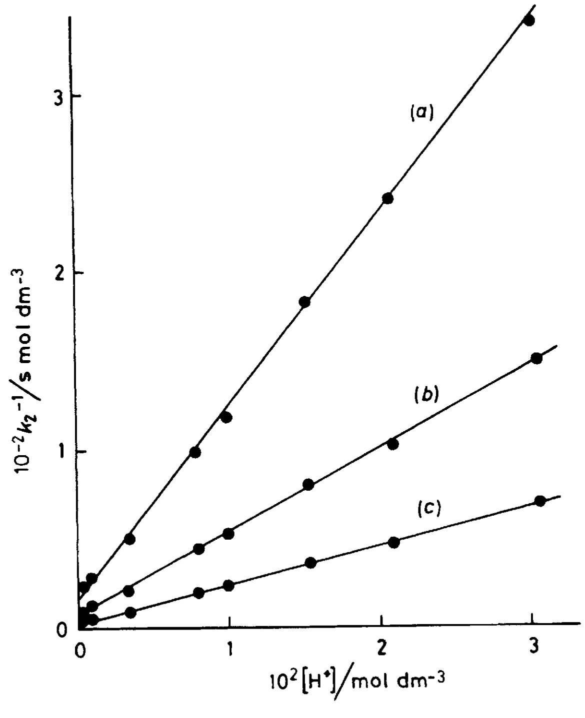

Figure 2. Plot of $1/k_2$ against $[H^+]$ for n-butylmalonic acid. Details as in Figure 1

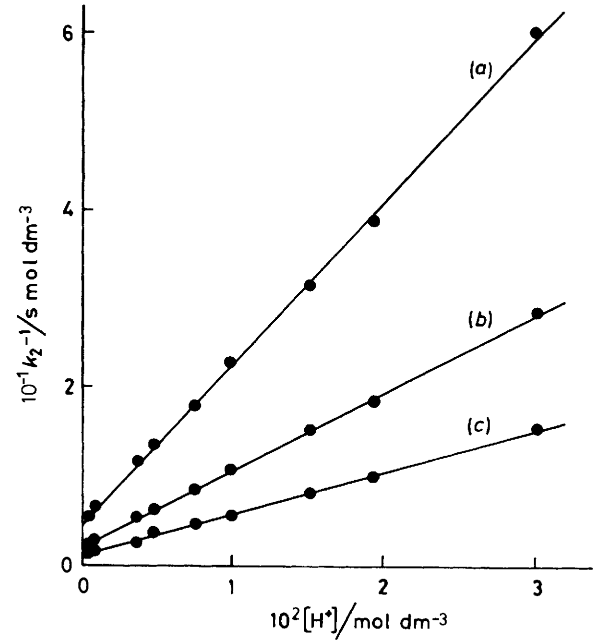

Figure 3. Plot of $1/k_2$ against $[H^+]$ for benzylmalonic acid. Details as in Figure 1

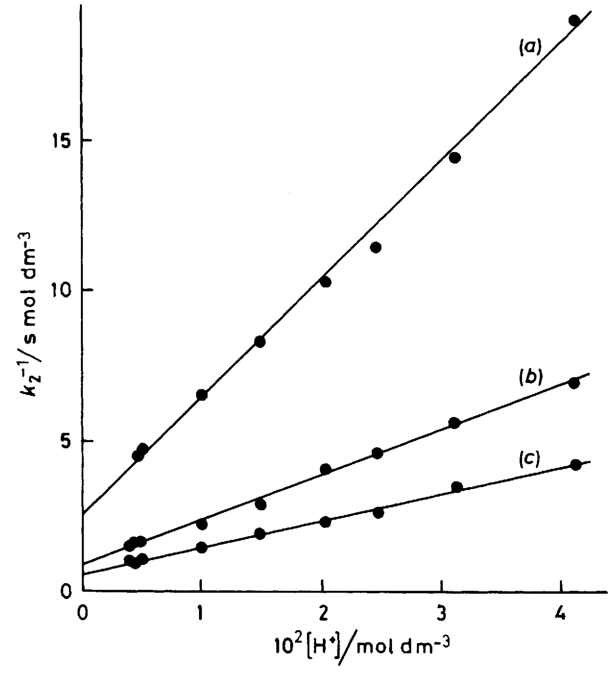

Figure 4. Plot of $1/k_2$ against $[H^+]$ for phenylmalonic acid at 15.0 (*a*), 25.0 (*b*), and 35.0 °C (*c*); $[Ir^{IV}] = 1.08 \times 10^{-4}$, $[H_2A]_T = 2.00 \times 10^{-2}$ mol dm^{-3}

the rate expression (6) can easily be derived on the basis of the oxidation mechanism proposed. Comparison of equation (6)

$$-\frac{d[Ir^{IV}]}{dt} = \frac{4kK_1[H_2A]_T[Ir^{IV}]}{K_1 + [H^+]} \qquad (6)$$

with (1) and (2) enables us to evaluate the rate constant k $(=1/4k_a)$ for the rate-determining step (4) and the first dissociation constant K_1 $(=1/4kk_b = k_a/k_b)$ of the dicarboxylic acids under examination. The estimated values of k and K_1 at three temperatures are also given in Table 2 together with the K_1 values obtained previously[11–13] at 25 °C by potentiometric titrations. If allowance is made for the different ionic strength in the case of phenylmalonic acid, the agreement between the two sets of K_1 values is satisfactory, providing further support to the validity of the treatment of kinetic data

Table 2. Kinetic data and first dissociation constants obtained at ionic strength 0.50 mol dm^{-3} and various temperatures

θ_c/°C	$10^{-1}k_a$/ s mol dm^{-3}	$10^{-3}k_b$/ s	10^2k/ dm^3 mol^{-1} s^{-1}	10^3K_1/mol dm^{-3} *a*	10^3K_1/mol dm^{-3} *b*
(*a*) Malonic acid					
25.0	27 ± 1	90 ± 3	0.093 ± 0.003	3.0 ± 0.1	2.4[11,12]
35.0	10.4 ± 0.4	32.6 ± 0.9	0.240 ± 0.009	3.2 ± 0.1	
45.0	4.5 ± 0.2	13.2 ± 0.5	0.55 ± 0.02	3.4 ± 0.2	
(*b*) n-Butylmalonic acid					
25.0	1.80 ± 0.08	10.1 ± 0.2	1.39 ± 0.06	1.78 ± 0.09	1.7[11,12]
35.0	0.72 ± 0.05	4.5 ± 0.1	3.5 ± 0.2	1.6 ± 0.1	
45.0	0.30 ± 0.01	2.08 ±0.05	8.3 ± 0.3	1.44 ± 0.06	
(*c*) Benzylmalonic acid					
25.0	0.46 ± 0.01	1.80 ± 0.02	5.4 ± 0.1	2.55 ± 0.06	2.5[11,12]
35.0	0.202 ± 0.005	0.86 ± 0.01	12.4 ± 0.3	2.35 ± 0.06	
45.0	0.105 ± 0.005	0.46 ± 0.01	24 ± 1	2.3 ± 0.1	
(*d*) Phenylmalonic acid					
15.0	0.28 ± 0.02	0.37 ± 0.01	8.9 ± 0.6	7.6 ± 0.6	4.0[c,12,13]
25.0	0.089 ± 0.005	0.147 ± 0.005	28 ± 2	6.0 ± 0.4	
35.0	0.065 ± 0.003	0.085 ± 0.003	38 ± 2	7.6 ± 0.4	

[a] This work. [b] By potentiometry. [c] At ionic strength 0.1 mol dm^{-3}.

Table 3. Enthalpies and entropies of activation for reaction (4) and thermodynamic parameters for reaction (3) at ionic strength 0.50 mol dm^{-3}

Substrate	$\Delta H^{\ddagger a}$/kJ mol^{-1}	$\Delta S^{\ddagger a}$/J K^{-1} mol^{-1}	$\Delta H_1^{\ominus a}$/kJ mol^{-1}	$\Delta S_1^{\ominus a,b}$/ J K^{-1} mol^{-1}
Malonic acid	68 ± 1	−76 ± 4	4.93 ± 0.01	−31.8 ± 0.3
n-Butylmalonic acid	67 ± 1	−53 ± 9	−8.3 ± 0.2	−80 ± 1
Benzylmalonic acid	58 ± 3	−75 ± 9	−5 ± 1	−66 ± 5
Phenylmalonic acid	49 ± 15	−92 ± 50	2 ± 9	−35 ± 30

[a] Estimated using a weighted least-squares method. [b] At 25.0 °C.

in the present work and, hence, of the reaction mechanism suggested.

Table 2 shows that the rate constant k is very sensitive to the substituent group present in malonic acid and that the rate of the electron-transfer process increases in the order: H_2mal < H_2bmal < H_2bzmal < H_2pmal. The observed dependence of k on the substituent group does not parallel the trend in the corresponding Taft substituent constants σ^*, but reflects the stabilization of the incipient radical of the transition state by hyperconjugation with the butyl and benzyl groups and by resonance with phenyl.[14,15] Thus the observed substituent effects upon the oxidation rate are also in agreement with the proposed rate-determining step (4).

As to the temperature dependence of the oxidation rates, the linear plot of log (k/T) against $1/T$ allows us to estimate (Table 3) the enthalpy and entropy of activation for the slow stage (4). The $\Delta S^{\ddagger}$ values are negative as expected for a reaction between two ions of the same charge. Moreover the activation enthalpy decreases on passing from H_2mal to H_2bmal, H_2bzmal, and H_2pmal and, consequently, the observed order of reactivity (H_2mal < H_2bmal < H_2bzmal < H_2pmal) is primarily determined by the decrease in this activation parameter. This is in accordance with the fact that the formation of a more stable radical implies a lower energy of activation.[15]

The values of the first dissociation constant K_1 obtained at three temperatures (Table 2) allow the evaluation of the thermodynamic parameters $\Delta S_1^{\ominus}$ and $\Delta H_1^{\ominus}$ (Table 3) for reaction (3). The values estimated by a kinetic method in the present work for malonic acid are in fair agreement with those reported[12] in the literature. For the remaining dicarboxylic acids the comparison cannot be made because, as far as we know, no values of these thermodynamic parameters are available. However, the present $\Delta H_1^{\ominus}$ and $\Delta S_1^{\ominus}$ data are similar to those obtained[12] for diethylmalonic acid and for cyclopropane-, cyclobutane-, and cyclopentane-1,1-dicarboxylic acids, the latter acids being considered as disubstituted malonic acids.

Acknowledgements

This work was supported by the 'Ministero della Pubblica Istruzione.'

References

1 A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 1954, 2456; K. K. Sen Gupta and S. Aditya, *Z. Phys. Chem. (Frankfurt)*, 1963, **38**, 25; J. J. Jwo and R. M. Noyes, *J. Am. Chem. Soc.*, 1975, **97**, 5422; Z. Amjad and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1977, 304.

2 T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1964, 1489, 1610, 3101; K. K. Sen Gupta and A. K. Chatterjee, *Z. Phys. Chem. (Frankfurt)*, 1971, **75**, 15 and refs. therein; B. S. Maritz and R. van Eldik, *Inorg. Chim. Acta*, 1976, **20**, 43; F. Mata and M.P. Alvarez, *Z. Phys. Chem. (Frankfurt)*, 1980, **120**, 155.

3 E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Phys. Chem.*, 1976, **80**, 2979; E. Mentasti, E. Pelizzetti, and C. Baiocchi, *J. Chem. Soc., Dalton Trans.*, 1977, 132; E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, 1978, **17**, 1181; K. K. Sen Gupta and U. Chatterjee, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2491; K. K. Sen Gupta, S. Maiti, U. Chatterjee, and T. Samanta, *Transition Met. Chem.*, 1982, **7**, 89; K. K. Sen Gupta, S. Maiti, T. Samanta, S. Nandi, and A. Banerjee, , *ibid.*, p. 274; W. D. Drury and J. M. DeKorte, *Inorg. Chem.*, 1983, **22**, 121.

4 R. Cecil, A. J. Fear, and J. S. Littler, *J. Chem. Soc. B*, 1970, 632.

5 H. N. Po, H. Eran, Y. Kim, and J. E. Byrd, *Inorg. Chem.*, 1979, **18**, 197; D. F. C. Morris and T. J. Ritter, *J. Chem. Soc., Dalton Trans.*, 1980, 216; H. N. Po, C. F. Lo, N. K. Jones, A. A. Galuska, and H. Eran, *J. Coord. Chem.*, 1981, **11**, 163.

6 K. K. Sen Gupta, U. Chatterjee, S. Maiti, P. K. Sen, and B. Bhattacharya, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1177 and refs. therein.

7 R. Cecil and J. S. Littler, *J. Chem. Soc. B*, 1968, 1420; R. Cecil, J. S. Littler, and G. Easton, *ibid.*, 1970, 626.

8 G. Arcoleo, F. P. Cavasino, E. Di Dio, and C. Sbriziolo, *J. Chem. Soc., Dalton Trans.*, 1980, 41 and refs. therein.

9 I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, 1962, **84**, 2032.

10 I. Heilbron and H. N. Bumbury, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1953, vol. 1, p. 262.

11 F. P. Cavasino and E. Di Dio, *J. Chem. Soc. A*, 1971, 3176.

12 A. E. Martell and R. M. Smith, 'Critical Stability Constants,' Plenum, New York, 1977, vol. 3.

13 E. Roletto, *J. Chim. Phys. Physicochim. Biol.*, 1974, **71**, 931.

14 G. Calvaruso, F. P. Cavasino, and C. Sbriziolo, *Int. J. Chem. Kinet.*, 1984, **16**, 1201.

15 R. T. Morrison and R. N. Boyd, 'Organic Chemistry,' 3rd edn., Allyn and Bacon, Boston, 1976.

Received 12*th November* 1984; *Paper* 4/1916