The Catalysis by Certain Metal Ions in the Bromination of 2-Carbethoxycyclopentanone

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In a previous paper [1], the effect of cupric and barium ions on the bromination of ethyl acetoacetate was examined. The two α-hydrogen atoms are replaced by bromine by two first order reactions which are both catalysed by bases in general (*e. g.* by water molecules or acetate ions). The rate-determining step is, in both changes, a proton transfer from the ester to the base. It was shown that the proton transfer from ethyl acetoacetate is catalysed by cupric ions while barium ions have only an insignificant influence. In order to explain this catalysis, it was assumed that a small amount of a complex between the cupric ion and the keto-form of ethyl acetoacetate exists in the solution. In such a complex, the proton is bound much more loosely than in the free ester, and the rate of transfer of protons to the base is, therefore, much greater.

In continuation of this examination, a study was made of the effect of different metal ions on the velocity of bromination of 2-carbethoxycyclopentanone,

$$\overline{(CH_2)_3COCHCOOC_2H_5} + Br_2 \rightarrow \overline{(CH_2)_3COCBrCOOC_2H_5} + H^+ + Br^- \qquad (1)$$

This β-keto-ester was chosen instead of ethyl acetoacetate because it has only one α-hydrogen atom for which reason no subsequent bromination takes place. The computation of the velocity constant is therefore both easier and more accurate. The kinetic behaviour of the two esters is, otherwise, qualitatively the same.

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MATERIALS AND PROCEDURE

Adipic acid was prepared from cyclohexanol by the procedure described in *Org. Syntheses* [2], except that stirring was made by a vigorous current of air instead of a mechanical stirrer. It is uncertain whether it is for this reason that the yield was greater and the product purer than stated in *Organic Syntheses*. By direct crystallisation was obtained 71 per cent of the theoretical amount (melting point 149.5° C), and by evaporation of the mother liquor was further gained 4 per cent (m. p. 147—149°).

Diethyl adipate was prepared from adipic acid and ethyl alcohol by the method of Micovic [3]. The yield was 84 per cent of the theoretical amount.

2-Carbethoxycyclopentanone was prepared by the following procedure which has been worked out by Professor Hakon Lund [4] who has kindly communicated it to me.

12 g of sodium is fused under toluene in a 500-ml round-bottomed flask. The flask is closed, shaken vigorously until the sodium solidifies to tiny balls, and is allowed to cool without the admission of air. It is then opened, and the toluene is decanted from the sodium which is washed by decantation with dry ether. 200 ml of dry ether and 75 g of diethyl adipate are now added. The flask is provided with a reflux condenser, and 1 ml of absolute alcohol is added to start the reaction. Now and then, the flask is shaken, especially when the reaction mixture gets thick. It is left till the next day when 35 ml of glacial acetic acid is added. The biggest lumps are mechanically disintegrated. When no more reaction is visible, sufficient water for dissolving the sodium acetate formed is added in small portions while the flask is cooled in ice water. The ether layer is washed with water and dried. The ether is evaporated, and the ester distilled under reduced pressure. The yield of ester boiling within 1° (boiling point 105° C/12 mm) at constant heat supply is 53 g or more than 90 per cent of the theoretical amount.

The 2-carbethoxycyclopentanone prepared in this way was purified by the following procedure. 80 g of crystalline cupric sulphate and 100 g of the ester were dissolved in water. The solution was neutralized with 2 molar ammonia (about 320 ml) which was added dropwise and with stirring. A precipitate of the cupric compound of the ester separated out. It was filtered and washed with water and with alcohol. It was then recrystallised from 96 per cent alcohol. Light-green crystals consisting of an alcoholate were obtained. They were dried at room temperature and, finally, at 100° C until all alcohol had evaporated. A mixture of 100 g of the dry cupric compound and 250 ml of 20 per cent hydrochloric acid was shaken and extracted once with 200 ml of ether and twice with 100 ml portions. The extract was dried with anhydrous sodium sulphate. The ether was removed by distillation. The ester was distilled through a Vigreux still-head in an all-glass apparatus. When the heat supply was kept constant, nearly all the preparation distilled at constant temperature (113° C/20 mm).

The inorganic substances used for the measurements were the purest commercial preparations, usually »for analysis». *Cupric nitrate, lead nitrate,* and *sodium perchlorate* were further recrystallised. In the *nickel nitrate* (for analysis), no cobalt, iron or heavy metals could be detected. Standard solutions of *zinc, cadmium,* and *manganous nitrate* were prepared by mixing equivalent amounts of solutions of the corresponding sulphates (for analysis) and barium nitrate (for analysis). A standard solution of *beryllium perchlorate* was prepared from solutions of beryllium sulphate and barium perchlorate. The beryllium sulphate had been prepared from pure beryllium oxide, and the barium perchlorate from barium hydroxide and perchloric acid (both for analysis). The solvents

for the bromination were prepared from standard solutions of the different substances. When necessary, the concentrations of the standard solutions were checked by analysis.

The procedure for the kinetic measurements was the same as in the previous paper [1]. It was sometimes noticed that a platinum electrode which had been in use for some time gave inaccurate results because it did not respond sufficiently quickly to changes in the redox potential of the solution. Two or three electrodes were therefore used alternately, and the measurement was approved only when different electrodes gave concordant results.

MEASUREMENTS IN SOLUTIONS CONTAINING STRONG ACIDS

A study was made of the effects of a series of salts on the rate of bromination in solvents containing either hydrochloric, nitric, or perchloric acid. In the presence of strong acid, the reaction always satisfied the first order law. The velocity constant k^* was calculated by means of the formula

$$k^*t = \log\ c - \log\ (c - \frac{x}{2})$$

where t is the time in minutes from the start of the reaction to the complete disappearance of the bromine, c the initial concentration of ester, and x the initial equivalent concentration of bromine. As velocity constant for a solution was taken the average of, as a rule, from 6 to 8 determinations with different initial concentrations of bromine. Table 1 illustrates the computation of k^* from the experimental data for two of the solutions.

Table 1. Bromination of 2-carbethoxycyclopentanone at 18.0° C.

0.003472	molar ester			0.003529	molar ester		
0.0200	molar KBr			0.0200	molar KBr		
0.0300	molar HNO_3			0.0300	molar HNO_3		
				0.04085	molar $Cu(NO_3)_2$		

Electrode	t	$\frac{x}{2}10^3$	k^*	Electrode	t	$\frac{x}{2}10^3$	k^*
a	3.18	0.799	0.03573	c	1.411	1.472	0.1661
b	5.30	1.226	0.03570	d	1.898	1.840	0.1686
a	7.10	1.536	0.03573	d	2.224	2.011	0.1647
b	9.77	1.916	0.03567	d	2.432	2.161	0.1692
a	12.46	2.226	0.03571	c	2.919	2.387	0.1679
b	16.85	2.593	0.03540	c	3.063	2.455	0.1687
b	18.81	2.723	0.03542	c	3.090	2.476	0.1700
		Mean	0.03562			Mean	0.1679

Table 2. Bromination of 2-carbethoxycyclopentanone (initial concentration 0.0035 molar) at 18.0° C in the solutions A to F containing, in addition, the substances given in the table (concentration c_S molar). k^* is the velocity constant, and k_S^* the increase of k^* per mole/liter of the substance.

		k^* (calc.)
A.	0.0200 M KBr	0.03542
B.	0.0200 M KBr + 0.0300 M HNO_3	0.03562
B_1.	0.0200 M KBr + 0.100 M HNO_3	0.03609
B_2.	0.0200 M KBr + 0.0100 M HNO_3	0.03549
C.	0.0200 M KBr + 0.0300 M HCl	0.03575
D.	0.0200 M KBr + 0.0300 M $HClO_4$	0.03527
D_1.	0.0200 M KBr + 0.100 M $HClO_4$	0.03492
E.	0.0200 M NaBr	0.03545
F.	0.0200 M NaBr + 0.0300 M $HClO_4$	0.03530

	c_S	k^*	k_S^*			c_S	k^*	k_S^*
	Aluminium nitrate					*Cupric nitrate*		
B_1	0.050	0.03553	— 0.0112		B	0.00513	0.0517	3.14
B_1	0.100	0.03416	— 0.0193		B	0.01028	0.0680	3.15
B	0.100	0.03455	— 0.0107		B [b]	0.01028	0.0677	3.12
B_2	0.100	0.03563	+ 0.0014		B_1	0.01028	0.0693	3.23
B_1 [a]	0.050	0.03364	— 0.0136		B	0.02057	0.1021	3.23
					B	0.04085	0.1679	3.24
	Barium chloride							
C	0.100	0.03704	0.0129					
C	0.200	0.03787	0.0106			*Diaquotetramminecobaltic*		
C	0.300	0.03860	0.0095			*nitrate*		
					B	0.0200	0.03552	— 0.005
	Beryllium perchlorate				B_1	0.0200	0.03574	— 0.018
D_1	0.0200	0.03425	— 0.0340					
D_1	0.0500	0.03320	— 0.0344					
D	0.0500	0.03367	— 0.0320			*Hexamminecobaltic nitrate*		
					B	0.0200	0.03470	— 0.046
	Cadmium nitrate							
B	0.0200	0.03685	0.062					
B	0.0600	0.03994	0.072			*Hydrochloric acid*		
					A	0.030	0.03578	0.0120
	Calcium chloride				A	0.100	0.03659	0.0117
C	0.0502	0.04042	0.0930		A	0.200	0.03760	0.0109
C	0.1003	0.04490	0.0912		A	0.300	0.03868	0.0109
C	0.2013	0.05401	0.0907					

[a] The solution contained, in addition, 0.150 M KNO_3.

[b] The initial concentration of ester was 0.0070 M instead of 0.0035 M.

Table 2 (continued)

	c_S	k^*	$k_S{}^*$		c_S	k^*	$k_S{}^*$
Lanthanum nitrate c)				*Perchloric acid*			
B	0.00497	0.0427	1.43	E	0.030	0.03522	— 0.0077
B	0.00996	0.0498	1.43	E	0.100	0.03500	— 0.0045
B	0.02001	0.0642	1.43	E	0.230	0.03444	— 0.0044
B	0.02139	0.0661	1.43	E	0.300	0.03410	— 0.0045
B₁	0.02139	0.0659	1.39				
B d)	0.02139	0.0652	1.41	*Potassium bromide*			
				B	0.030	0.0350	— 0.021
Lead nitrate							
B	0.0250	0.04194	0.253	*Potassium chloride*			
B	0.0499	0.04845	0.257	C	0.100	0.03502	— 0.0073
B	0.1000	0.06054	0.249	C	0.200	0.03420	— 0.0078
Magnesium perchlorate				*Potassium nitrate*			
D	0.0400	0.03741	0.0535	B	0.100	0.03454	— 0.0108
D	0.1000	0.04058	0.0531	B	0.200	0.03322	— 0.0120
D	0.2000	0.0458	0.0527				
				Sodium chloride			
Manganous nitrate				C	0.100	0.03514	— 0.0061
B	0.0194	0.03818	0.132	C	0.200	0.03456	— 0.0060
B	0.0583	0.04473	0.156				
B₁	0.0583	0.04480	0.149	*Sodium nitrate*			
				B	0.100	0.03464	— 0.0098
Nickel nitrate				B	0.200	0.03350	— 0.0106
B	0.00993	0.0566	2.11				
B	0.01995	0.0783	2.14	*Sodium perchlorate*			
B₁	0.01995	0.0787	2.14	F	0.100	0.03289	— 0.0241
B	0.04963	0.1425	2.15	F	0.200	0.03090	— 0.0220
B	0.09974	0.2475	2.12				
				Zinc nitrate			
Nitric acid				B	0.01980	0.04605	0.527
A	0.030	0.03562	0.0067	B	0.04962	0.06241	0.540
A	0.100	0.03591	0.0049	B₁	0.04962	0.06198	0.522
A	0.200	0.03661	0.0060	B	0.0991	0.0896	0.545
A	0.300	0.03739	0.0066				

c) Lanthanum nitrate purified through the oxalate was used only for the first three determinations.

d) The solution contained 0.05 M KBr instead of 0.02 M KBr.

Table 2 gives a general view of the results obtained. The 23 substances examined are arranged alphabetically. The solvents to which they were added are denoted by the letters from A to F. Their composition and the corresponding velocity constant are given at the top of the table. When $\triangle k^*$ is the in-

crease of k^* due to the addition of the substance S in the concentration c_S molar, the effect of S may be expressed by the ratio $k_S^* = \triangle k^*/c_S$. For most of the substances examined k_S^* is independent of c_S. Only four of the substances, namely cupric, nickel, lanthanum, and zink nitrate, have considerable effects, from 90 to 15 per cent increase in 0.01 molar solution. Moderate increases of the rate are found for the following five salts: lead nitrate, manganous nitrate, cadmium nitrate, calcium chloride, and magnesium perchlorate. The rest of the substances examined have very small, positive or negative, effects.

In some cases, the same substance was examined in solvents with different concentrations of strong acid. If the effect of the salt were partly a basic catalysis by a hydroxy-metal ion formed by dissociation of the hydrated metal ion, k_S^* would decrease when the concentration of strong acid is increased. A decrease of k_S^* was found for aluminium nitrate and diaquotetrammine-cobaltic nitrate in which cases it is known that hydroxy-metal ions are formed. For the other salts, no or only an insignificant change of k_S^* was found.

Table 3.

S	k_S^* found	k_S^* calc.	S	k_S^* found	k_S^* calc.
HCl	0.0111	0.0110	NaNO$_3$	— 0.0103	— 0.0105
HNO$_3$	0.0061	0.0067	NaClO$_4$	— 0.0227	— 0.0222
HClO$_4$	— 0.0046	— 0.0055	KCl	— 0.0076	— 0.0075
NaCl	— 0.0060	— 0.0062	KNO$_3$	— 0.0116	— 0.0118

In Table 3 are presented the average values of k_S^* found for the three strong acids and their sodium and potassium salts. The table shows that k_S^* is an additive property of the ions. If we arbitrarily take the effect of the potassium ion as zero, the best agreement is obtained when we for the other ions involved choose the values given in Table 4. From these values we calculate k_S^* given in the last column of Table 3.

The molar effects of the other ions examined may now be calculated from the experimental data together with the molar effects of the anions when it is assumed that no complex formation between the metal ions and the anions present takes place. This assumption is supported by the fact that k_S^* in general is independent of c_S. There is however one case where it does not hold. It is known that cadmium ions to a considerable extent form complexes with bromide ions [5]. Data for the calculation of the cadmium-ion concentration in the two solutions examined are not available. It may only be very

Table 4. Bromination of 2-carbethoxycyclopentanone at 18.0° C in solutions containing strong acid.

$$k^* = 0.03500 + \Sigma k_I^* c_I$$

The values in parentheses are approximate.

I	k_I^*	I	k_I^*
Cu^{++}	3.17	Be^{++}	0.014
Ni^{++}	2.15	Al^{+++}	(0.01)
La^{+++}	1.47	$Co(NH_3)_4(H_2O)_2^{+++}$	(0.01)
Zn^{++}	0.55	Na^+	0.0013
Pb^{++}	0.28	K^+	*0.0000*
Mn^{++}	0.17	$Co(NH_3)_6^{+++}$	— 0.01
Cd^{++}	(0.1—0.2)		
Mg^{++}	0.111	Cl^-	— 0.0075
Ca^{++}	0.106	NO_3^-	— 0.0118
Ba^{++}	0.028	Br^-	— 0.021
H^+	0.0185	ClO_4^-	— 0.0235

roughly estimated that, in the first solution, nearly one half and, in the second, about one fourth of the cadmium ions are bound to bromide ions. When a complex formation of this magnitude is taken into account, we find that the molar effect of the cadmium ion is between 0.1 and 0.2. The molar effects of all the ions examined are given in table 4. The velocity constant in a solution of these ions may be expressed by the formula

$$k^* = 0.03500 + \Sigma k_I^* c_I \qquad (2)$$

where k_I^* is the molar effect and c_I the concentration of the ion I, and the summation includes all the ions present in the solution. The velocity constants for the solvents A to F given at the top of Table 2 have been calculated by means of this formula. They have been used for the calculation of k_S^* given in the table. The velocity constants for the solvents B, B_1, C, and F have also been measured directly. They may be found in the table under the headings nitric, hydrochloric, and perchloric acid.

MEASUREMENTS IN ACETATE BUFFER SOLUTIONS

In the previous part of this paper, we have examined the effects of a series of metal ions on the rate of bromination in solutions containing strong acids. In this part, we shall study the effects of two of them, cupric and nickel ions, when the reaction takes place in acetate buffer solutions.

When cupric ions are present, the following differential equation holds

$$\frac{d\left(c - \frac{x}{2}\right)}{dt} = \left[k_{\mathrm{r}} + k_{\mathrm{Cu}^{++}}\, c_{\mathrm{Cu}^{++}} + k_{\mathrm{Ac}^-}\, c_{\mathrm{Ac}^-} + k_{\mathrm{Cu}^{++}\,\mathrm{Ac}^-}\, c_{\mathrm{Cu}^{++}}\, c_{\mathrm{Ac}^-}\right]\left(c - \frac{x}{2}\right) \quad (3)$$

In this equation, k_{r} includes k_0, the velocity constant in pure water, and the effects of all the ions present except the cupric and the acetate ion. Owing to the production of hydrogen ions by the bromination (scheme 1) and to complex formation between cupric and acetate ions, both the acetate- and cupric-ion concentration change during the reaction. These changes are approximately proportional to the concentration of hydrogen bromide formed $\left(= \frac{x}{2}\right)$. We, therefore, may write

$$c_{\mathrm{Ac}^-} = c_{\mathrm{Ac}^-(\infty)} + p\left(c - \frac{x}{2}\right) \quad (4)$$

$$c_{\mathrm{Cu}^{++}} = c_{\mathrm{Cu}^{++}(\infty)} - q\left(c - \frac{x}{2}\right) \quad (5)$$

When these expressions are introduced into equation 3, we obtain by integration

$$k_{(\infty)}{}^* t = \frac{n+l}{2n} \log \frac{\dfrac{n-l}{2m} + \left(c - \dfrac{x}{2}\right)}{\dfrac{n-l}{2m} + c} + \frac{n-l}{2n} \log \frac{\dfrac{n+l}{2m} - \left(c - \dfrac{x}{2}\right)}{\dfrac{n+l}{2m} - c} - \log \frac{c - \dfrac{x}{2}}{c} \quad (6)$$

where

$$k_{(\infty)}{}^* = k_{\mathrm{r}}{}^* + k_{\mathrm{Cu}^{++}}{}^*\, c_{\mathrm{Cu}^{++}(\infty)} + k_{\mathrm{Ac}^-}{}^*\, c_{\mathrm{Ac}^-(\infty)} + k_{\mathrm{Cu}^{++}\mathrm{Ac}^-}{}^*\, c_{\mathrm{Cu}^{++}(\infty)}\, c_{\mathrm{Ac}^-(\infty)} \quad (7)$$

$$l = p\left[k_{\mathrm{Ac}^-} + k_{\mathrm{Cu}^{++}\mathrm{Ac}^-}\, c_{\mathrm{Cu}^{++}(\infty)}\right] - q\left[k_{\mathrm{Cu}^{++}} + k_{\mathrm{Cu}^{++}\mathrm{Ac}^-}\, c_{\mathrm{Ac}^-(\infty)}\right] \quad (8)$$

$$m = pq\, k_{\mathrm{Cu}^{++}\mathrm{Ac}^-} \quad (9)$$

$$n = \sqrt{l^2 + 4k_{(\infty)}\, m} \quad (10)$$

p and q are found by introducing $c_{\mathrm{Ac}^-(0)}$ and $c_{\mathrm{Cu}^{++}(0)}$ corresponding to $t = 0$ and $x = 0$ into equation 4 and 5. In computing $k_{(\infty)}{}^*$ by means of equation 6, it is necessary to use a method of successive approximations since $k_{(\infty)}{}^*$ enters into both sides of the equation.

In the calculation of the acetate and cupric ion concentrations corresponding to the times 0 and ∞, we have used values found in a previous paper [6]

for the dissociation constant of acetic acid, K_{HAc}, and for the complexity constants

$$K_1 = c_{\text{Cu}^{++}} c_{\text{Ac}^-}/c_{\text{CuAc}^+} \text{ and } K_2 = c_{\text{Cu}^{++}} c_{\text{Ac}^-}^2/c_{\text{CuAc}_2}$$

They may be expressed by the following formulae where μ is the ionic strength of the solution

$$-\log K_{\text{HAc}} = 4.7595 - 0.996\sqrt{\mu} + 1.15\mu - 0.8\mu^2 + 0.035\,c_{\text{HAc}} - 0.25\,c_{\text{Ac}^-} \quad (11)$$

$$\log K_1 = 2.164 - 1.992\sqrt{\mu} / (1 + 1.8\sqrt{\mu}) \quad (12)$$

$$\log K_2 = 3.205 - 2.988\sqrt{\mu} / (1 + 2\sqrt{\mu}) \quad (13)$$

When the buffer solution contains nickel instead of cupric ions, we may use the same system of formulae if only Cu^{++} is replaced by Ni^{++}, but here no data are available for the calculation of the degree of complex formation. The following observation indicates, however, that no, or only a very slight, complex formation between nickel and acetate ions takes place in dilute solutions. When 25 ml of each of the four solutions (a) 0.1 M $\text{Ni(NO}_3)_2$, (b) 0.1 M $\text{Ni(NO}_3)_2$ + 0.1 M HAc, (c) 0.1 M $\text{Ni(NO}_3)_2$ + 0.1 M HAc + 0.2 M NaAc, and (d) 0.1 M $\text{Ni(NO}_3)_2$ + 0.1 M HAc + 0.5 M NaAc were placed in test tubes of the same size, no difference in colour could be seen by the naked eye in the first three solutions while it was just possible to distinguish a displacement in solution (d).

The solutions used for the kinetic measurements were much more dilute (see Table 8). It therefore seems to be permissible to neglect the complex formation between nickel and acetate ions. When the nickel ion concentration is constant throughout the reaction we obtain instead of equation 6

$$k_{(\infty)}{}^* t = \log \frac{\dfrac{k_{(\infty)}}{p\,(k_{\text{Ac}^-} + k_{\text{Ni}^{++}\text{Ac}^-}\,c_{\text{Ni}^{++}})} + (c - \dfrac{x}{2})}{\dfrac{k_{(\infty)}}{p\,(k_{\text{Ac}^-} + k_{\text{Ni}^{++}\text{Ac}^-}\,c_{\text{Ni}^{++}})} + c} - \log \frac{c - \dfrac{x}{2}}{c} \quad (14)$$

In order to see which influence a possible complex formation may have, the velocity constants have been computed both on the assumption that complex formation may be neglected (formula 14) and on the assumption that an ion NiAc^+ with a complexity constant $K_1 = 10$ is formed (formula 6).

The acetate-ion catalysis. Measurements were carried out in four acetate buffer solutions of the compositions given in Table 5. The experimental data

Table 5. Bromination of 2-carbethoxycyclopentanone at 18.0° C in acetate buffer solutions. The initial molar concentrations of the solutions are given in the first five lines of the table.

	I	II	III	IV
HAc	0.0200	0.0200	0.0400	0.0200
NaAc	0.00598	0.01000	0.01000	0.01600
NaNO$_3$	0.0740	0.0700	0.0700	0.0640
KBr	0.0200	0.0200	0.0200	0.0200
Ester	0.003623	0.003623	0.003623	0.003623
$K_{HAc}\ 10^5$	2.80	2.79	2.78	2.77
$c_{H^+(0)}\ 10^5$	9.2	5.5	11.0	3.4
$c_{H^+(\infty)}\ 10^5$	25.1	10.1	18.4	5.2
$c_{Ac^-(0)}$	0.00607	0.01006	0.01011	0.01603
$c_{Ac^-(\infty)}$	0.00261	0.00648	0.00656	0.01243
$k_{(\infty)}*$	0.06236	0.1036	0.1045	0.1669
k_r*	0.03466	0.0347	0.0347	0.0348
$k_{Ac^-}*$	10.61	10.63	10.64	10.63

for one of the solutions are presented in more detail in Table 6. The velocity constant $k_{(\infty)}*$ has been calculated by means of formula 14 ($c_{Ni^{++}} = 0$). $k_{Ac^-}*$ given in the last line of Table 5 has been computed from $k_{(\infty)}*$ by means of the equation $k_{(\infty)}* = k_r* + k_{Ac^-}*\ c_{Ac^-(\infty)}$, where k_r* has been calculated from the data in Table 4. There is a good agreement between the values of $k_{Ac^-}*$ found for the four solutions. The average is $k_{Ac^-}* = 10.63$.

The combined cupric- and acetate-ion catalysis. Measurements were carried out in five acetate buffer solutions containing cupric nitrate. The compositions of the solutions are given in Table 7. The experimental data for one of the

Table 6. Experimental data.

Solution IV (Table 5)			Solution IX (Table 7)		
t	$\frac{x}{2}10^3$	$k_{(\infty)}*$	t	$\frac{x}{2}10^3$	$k_{(\infty)}*$
0.902	1.224	0.1671	0.835	1.471	0.2176
1.240	1.527	0.1630	0.849	1.486	0.2170
1.522	1.777	0.1650	1.091	1.791	0.2212
1.976	2.120	0.1680	1.162	1.860	0.2201
2.062	2.170	0.1675	1.566	2.209	0.2173
2.296	2.315	0.1687	1.576	2.223	0.2184
2.684	2.515	0.1693	1.975	2.486	0.2158
	Mean	0.1669	2.129	2.578	0.2161
				Mean	0.2179

Table 7. Bromination of 2-carbethoxycyclopentanone at 18.0° C in acetate buffer solutions containing cupric nitrate. The initial molar concentrations of the solutions are given in the first six lines of the table.

	V	VI	VII	VIII	IX
HAc	0.1000	0.02000	0.02000	0.02000	0.01000
NaAc	0.00996	0.00598	0.01000	0.01000	0.00997
$NaNO_3$	0.0500	0.0540	0.0500	0.0600	0.0500
KBr	0.0200	0.0200	0.0200	0.0200	0.0200
$Cu(NO_3)_2$	0.01023	0.01023	0.01023	0.005115	0.01023
Ester	0.003603	0.003623	0.003623	0.003584	0.003603
$K_{HAc}\ 10^5$	2.80	2.83	2.82	2.80	2.82
K_1	56.8	56.4	56.8	57.4	56.8
K_2	412	408	412	418	412
$c_{H^+(0)}\ 10^5$	39.0	13.7	8.0	6.7	4.1
$c_{H^+(\infty)}\ 10^5$	61.5	38.3	15.1	12.5	8.8
$c_{Ac^-(0)}$	0.007130	0.004088	0.006931	0.008256	0.006880
$c_{Ac^-(\infty)}$	0.004691	0.001717	0.004377	0.005273	0.004325
$c_{Cu^{++}(0)}$	0.007161	0.008258	0.007225	0.003401	0.007241
$c_{Cu^{++}(\infty)}$	0.008022	0.009318	0.008143	0.003892	0.008163
$\mu_{(0)}$	0.1047	0.1068	0.1046	0.1019	0.1046
$\mu_{(\infty)}$	0.1068	0.1092	0.1066	0.1030	0.1066
$k_{(\infty)}*$	0.2182	0.1278	0.2108	0.1671	0.2179
k_r*	0.03468	0.03462	0.03468	0.03469	0.03468
$k_{Cu^{++}}*c_{Cu^{++}(\infty)}$	0.02543	0.02954	0.02581	0.01234	0.02588
$k_{Ac^-}*c_{Ac^-(\infty)}$	0.04987	0.01825	0.04653	0.05605	0.04597
$k_{Cu^{++}Ac^-}*c_{Cu^{++}(\infty)}c_{Ac^-(\infty)}$	0.1082	0.0454	0.1038	0.0640	0.1114
$k_{Cu^{++}Ac^-}*\ 10^{-3}$	2.88	2.84	2.91	3.12	3.16

solutions are presented in more detail in Table 6. The velocity constant $k_{(\infty)}*$ has been calculated by means of formula 6. It may be expressed as a sum of four terms by means of equation 7. The first three terms may be calculated from the data given earlier in this paper. When they are subtracted from $k_{(\infty)}*$, we find the last term of the expression, and from this again $k_{Cu^{++}Ac^-}*$ given in the last line of table 7. The values of $k_{Cu^{++}Ac^-}*$ found for the first three and for the last two of the solutions agree well among themselves, but the latter group has given somewhat higher results than the former. The average of all five values is 2.98×10^3. $k_{Cu^{++}Ac^-}*$ is the bimolecular velocity constant for a reaction between two ions of opposite sign. According to Brønsted [7], it will therefore decrease with increasing ionic strength. The ionic strengths of the solutions examined are, however, nearly the same. The differences are so small that they can have no importance for the constancy of $k_{Cu^{++}Ac^-}*$.

The combined nickel- and acetate-ion catalysis. Measurements were carried out in four acetate buffer solutions containing nickel nitrate. The compositions of the solutions are given in Table 8. The experimental data for one of the solutions are presented in more detail in Table 9. The velocity constant $k_{(\infty)}*$ has been calculated (a) on the assumption that complex formation between nickel and acetate ions may be neglected, and (b) on the assumption that the ion $NiAc^+$ is the only complex formed and that its complexity constant is $K_1 = 10$. When $k_{(\infty)}*$ is expressed by an equation analogous to equation 7, we find the values of $k_{Ni^{++}+Ac^-}*$ given in table 8. While $k_{(\infty)}*$ increases only 1 per cent when we make assumption (b) instead of (a), $k_{Ni^{++}+Ac^-}*$ increases considerably. There is a moderately good agreement between the values of $k_{Ni^{++}+Ac^-}*$

Table 8. *Bromination of 2-carbethoxycyclopentanone at 18.0° C in acetate buffer solutions containing nickel nitrate. The initial molar concentrations of the solutions are given in the first six lines of the table.*

	X	XI	XII	XIII
HAc	0.0200	0.0600	0.0200	0.0200
NaAc	0.00996	0.00996	0.005955	0.005955
NaNO$_3$	0.0500	0.0500	0.0540	0.0340
KBr	0.0200	0.0200	0.0200	0.0200
Ni(NO$_3$)$_2$	0.009934	0.009934	0.009934	0.01987
Ester	0.003603	0.003603	0.003591	0.003603

a) Complex formation neglected:

	X	XI	XII	XIII
μ	0.1099	0.1100	0.1100	0.1198
$K_{HAc}\ 10^5$	2.82	2.81	2.83	2.86
$c_{H^+(0)}10^5$	5.6	16.7	9.3	9.4
$c_{H^+(\infty)}10^5$	10.3	26.9	25.2	25.6
$c_{Ac^-(0)}$	0.01002	0.01013	0.006048	0.006049
$c_{Ac^-(\infty)}$	0.006460	0.006626	0.002616	0.002608
$k_{(\infty)}*$	0.2238	0.2243	0.1275	0.1855
k_r*	0.03467	0.03467	0.03463	0.03460
$k_{Ni^{++}}*\,c_{Ni^{++}}$	0.02136	0.02136	0.02136	0.04272
$k_{Ac^-}*\,c_{Ac^-(\infty)}$	0.06867	0.07043	0.02781	0.02772
$k_{Ni^{++}+Ac^-}*\,c_{Ni^{++}}c_{Ac^-(\infty)}$	0.0991	0.0978	0.0437	0.0805
$k_{Ni^{++}+Ac^-}*\,10^{-3}$	1.54	1.49	1.68	1.55

b) Complexity constant $K_1 = 10$:

	X	XI	XII	XIII
$c_{Ac^-(0)}$	0.009185	0.009296	0.005536	0.005101
$c_{Ac^-(\infty)}$	0.005914	0.006079	0.002405	0.002220
$c_{Ni^{++}(0)}$	0.009098	0.009089	0.009413	0.01890
$c_{Ni^{++}(\infty)}$	0.009379	0.009364	0.009701	0.01944
$k_{(\infty)}*$	0.2257	0.2264	0.1286	0.1880
$k_{Ni^{++}+Ac^-}*\,10^{-3}$	1.95	1.88	2.04	1.88

Table 9. Experimental data for solution X (Table 8).

t	$\frac{x}{2} 10^3$	$k_{(\infty)} *^{a)}$	$k_{(\infty)} *^{b)}$
0.921	1.630	0.2170	0.2193
1.121	1.889	0.2234	0.2255
1.265	2.036	0.2239	0.2259
1.461	2.215	0.2246	0.2266
1.767	2.541	0.2258	0.2275
1.832	2.500	0.2269	0.2286
2.345	2.776	0.2253	0.2268
	Mean	0.2238	0.2257

[a)] Complex formation between nickel and acetate ions neglected.
[b)] It has been assumed that the complexity constant of the ion $NiAc^+$ is 10.

found for the four solutions. The average is 1.57×10^3 when complex forma-
tion is neglected, while it is 1.94×10^3 when it is assumed that $K_1 = 10$.
The values agree only slightly better among themselves in case (b) than in
case (a), and there is no reason to expect a better agreement for another value
of K_1. The constancy of the colour of a dilute nickel nitrate solution when
acetate ions are added, seems to show that no, or only a very small, complex
formation takes place. We therefore consider 1.57×10^3 to be the most
reliable value of the constant $k_{Ni^{++}Ac^-}*$.

DISCUSSION

According to the theory developed in earlier papers [8,9], the rate-determin-
ing step in the bromination of β-keto-esters is a proton transfer from the ester
to the catalysing base (*e. g.* water or acetate ions). It has now been found that
certain metal ions accelerate both the water reaction and the acetate-ion
catalysis. The effect of the metal ions may be interpreted as a catalysis of
the proton transfer from the ester to the base. As seen from Table 10, cupric
ions increase the velocity of proton transfer from ethyl acetoacetate to water
molecules and to acetate ions by nearly the same factor, while, in the bromina-
tion of 2-carbethoxycyclopentanone, cupric and nickel ions have effects on
the transfer to acetate ions which are, respectively, 3.1 and 2.4 times as great
as their effects on the transfer to water molecules. In order to explain the
metal-ion catalysis, it is assumed that a small amount of a complex between
the metal ion and the keto-form of the ester exists in the solution. In such a
complex, the proton is bound much more loosely than in the free ester, and the

Table 10. Comparison of the effects of metal ions ($Me^{++} = Cu^{++}$ or Ni^{++}) on the velocity of proton transfer to water molecules and to acetate ions.

$$r_0 = k_{Me^{++}}/k_0 \text{ and } r_{Ac^-} = k_{Me^{++} Ac^-}/k_{Ac^-}$$

	$k_0{}^*$	$k_{Ac^-}{}^*$	Me^{++}	r_0	r_{Ac^-}	$\dfrac{r_{Ac^-}}{r_0}$
Ethyl acetoacetate [1]	0.01855	8.21	Cu^{++}	145	139	1.0
Carbethoxycyclopentanone	0.03500	10.63	Cu^{++}	90.6	280	3.1
			Ni^{++}	61.4	148	2.4

rate of transfer of protons to the base is, therefore, much greater. While no other experimental facts indicate the existence of complexes between metal ions and the keto-forms of β-keto-esters, it is known that their (enolic) anions, and other anions of a similar structure, combine with certain metal ions. Mellor and Maley [10] have recently determined the stabilities of the complexes formed between the anion of salicylaldehyde and eight divalent metal ions in the solvent 50 per cent dioxane — 50 per cent water. They found that the stability constant of the complex decreases in the order: Pd^{++}, Cu^{++}, Ni^{++}, Pb^{++}, Co^{++}, Cd^{++}, Zn^{++}, Mg^{++}. The catalysis by six of these ions has been examined in this paper. It was found that the effect decreases in the same order, except that Zn^{++} comes between Ni^{++} and Pb^{++}.

SUMMARY

The rate of bromination of 2-carbethoxycyclopentanone was measured in solutions containing strong acids and, in addition, different electrolytes. It was found that certain metal ions catalyse the reaction. The catalytic effect decreases in the order: Cu^{++}, Ni^{++}, La^{++}, Zn^{++}, Pb^{++}, Mn^{++}, Cd^{++}, Mg^{++}, Ca^{++}. The rest of the ions examined: H^+, Na^+, K^+, Ba^{++}, Be^{++}, Al^{+++}, $Co(NH_3)_6{}^{+++}$, $Co(NH_3)_4(H_2O)_2{}^{+++}$, Cl^-, Br^-, $NO_3{}^-$, and $ClO_4{}^-$, have only very small, positive or negative, effects.

The reaction was also studied in acetate buffer solutions with and without added cupric or nickel nitrate. The catalytic effects of the acetate, cupric, and nickel ion were determined.

The velocity of the base-catalysed bromination of β-keto-esters is a measure of the rate of proton transfer from the ester to the base (e. g. water or acetate ion). It follows from the measurements in this and a previous paper [1], that certain metal ions catalyse the proton transfer. In order to explain this catalysis, it is assumed that a small amount of a complex between the metal ion

and the keto-form of the ester exists in the solution. In such a complex, the proton is bound much more loosely than in the free ester, and the rate with which it is transferred to a base is, therefore, much greater.

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