

The Cupric-Ion Catalysis in the Bromination of Ethyl Acetoacetate

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When bromine water is added to an aqueous solution of ethyl acetoacetate the following consecutive reactions take place



They are of the first order with respect to the esters, and the rate is independent of the concentration of bromine. Both reactions are catalysed by bases in general, *i. e.* by molecules that can take up a proton, and the catalytic power of a base increases with increasing basic strength. The rate-determining step is, therefore, a bimolecular proton transfer from the ester to the base. Also water molecules act as proton acceptors. When no basic catalyst is added, the rate measured is exclusively that of the proton transfer to the water molecules of the solvent. The bromination of ethyl acetoacetate was studied experimentally, and the theory of the basic catalysis given in earlier papers ^{1, 2, 3}. In this paper it is shown that, if also cupric ions are added, an additional acceleration of reaction 1 is found. The effect of cupric ions appears as a catalysis of the bimolecular proton transfer from the ethyl acetoacetate to the base. When the medium contains both cupric ions and a base B, the first order velocity constant of reaction 1 may therefore be written

$$k = k_0 + k'_0 c_{\text{Cu}^{++}} + k_{\text{B}} c_{\text{B}} + k'_{\text{B}} c_{\text{Cu}^{++}} c_{\text{B}} \quad (3)$$

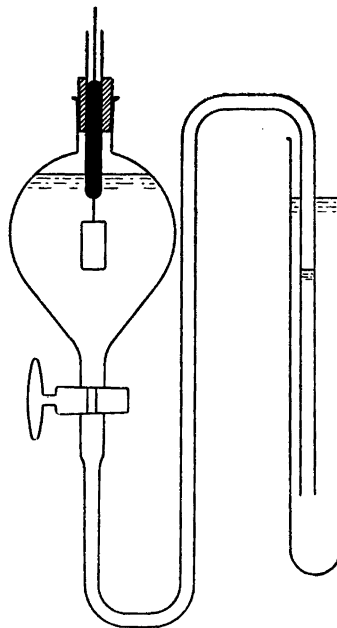


Fig. 1. Reaction vessel.

PROCEDURE AND MATERIALS

As reaction vessel served a separatory funnel with glass stopper and a long stem bent as shown in Fig. 1. The stem and the bore of the stopcock were first filled with a solution of the same composition as the reacting mixture but without ester and bromine. The funnel was then charged with solution of the ester and the other substances for the experiment except bromine. It was placed in a water thermostat at 18.0° C. The end of the stem was dipping into a test tube with 3.5 molar potassium chloride forming the connexion to a calomel electrode. A weight burette with bromine water⁴ was also placed in the thermostat. When temperature equilibrium was attained the weight burette and the reaction vessel were taken out, and bromine water, insufficient for completing the reaction, was quickly added to the solution in the funnel which was again placed in the thermostat. The total volume of the reacting mixture was always 125 ml. When most of the bromine had reacted, the glass stopper was replaced by a cork carrying a bright platinum electrode, and the stopcock was opened (see Fig. 1). The solution always contained 0.02 molar potassium bromide which secured a well defined potential of the cell. A valve potentiometer (maker «Radiometer», Copenhagen) had, beforehand, been so adjusted that its galvanometer would give no deflection when about 10^{-6} molar bromine was left in the reaction vessel. With an initial ester concentration of 0.004 molar, this corresponds to only 0.0125 per cent of the bromine necessary for complete bromination. The moment when all the free bromine had disappeared was therefore indicated by a quick change of sign of the deflection of the galvanometer. By repeating the experiment with different initial concentrations of bromine, it was possible to follow the reaction kinetically.

The ethyl acetoacetate used for the measurements was an old preparation which had 15 years before been purified through the sodium hydrogen sulphite compound^{1, 2}. The bromine water was prepared from Kahlbaum's bromine »for analysis». The other substances used were the purest commercial preparations. The cupric nitrate had further been recrystallized from water.

THE CUPRIC-ION CATALYSIS OF THE WATER REACTION

The bromination was studied in 0.002 molar hydrochloric acid and in the same solution containing, in addition, barium or cupric nitrate. When c is the initial molar concentration of the ester, x the equivalent concentration of bromine used by the reaction at the time t minutes after the start, k and h the first order velocity constants of, respectively, reaction 1 and 2, the following formula holds^{1, 2}

$$c - \frac{x}{4} = c \left[A 10^{-k^*t} - \left(A - 1 + \frac{\varepsilon}{2} \right) 10^{-h^*t} \right] \quad (4)$$

where $A = (1 - \varepsilon) \left(1 + \frac{h^*}{2(h^* - k^*)} \right)$

and ε ($= 0.0037$) is the degree of enolisation^{1, 2} of ethyl acetoacetate at equilibrium in the solution. An asterisk denotes that the factor $\log e$ has been omitted, thus $k^* = 0.4343 k$. The method^{1, 2} used for computing the velocity constants is very time-consuming. An easier and very ingenious method for the analysis of irreversible consecutive first order reactions has been worked out by Swain⁴. His paper was, however, not yet available here when the computations were carried out.

The results of the measurements and computations are given in Tables 1 and 2. Table 1 shows that a good agreement with formula 4 is obtained when the values of k^* and h^* given in Table 2 are chosen. The accuracy with which the two constants may be determined from a given set of measurements depends upon the ratio h^*/k^* . The smaller of the two constants may always be estimated most accurately. When no cupric nitrate is present, h^* is about 11 times as great as k^* which ratio allows a good determination of k^* but only a moderate estimate of h^* . When cupric nitrate is added, the ratio decreases and, consequently, the degree of uncertainty in k^* increases.

It is seen from Table 2 that k^* rises considerably when cupric nitrate is added while h^* does not change appreciably (considering the smaller accuracy of its estimation). The increase of k^* is proportional to the concentration C of cupric nitrate. The measurements with barium nitrate show that this salt has no, or only a slight, effect on the two constants. The effect of cupric

Table 1. Bromination of ethyl acetoacetate (0.003896 molar) at 18.0° C in solutions containing 0.0020 M HCl, 0.020 M KBr, and the salts given below. The table shows x (gram-equivalents of bromine per liter which had reacted t minutes after the start) found by experiment and calculated from formula 4 when the values of k^* and h^* given in Table 2, and $\epsilon = 0.0037$ are used.

t	$x10^3$ found	$x10^3$ calc.	t	$x10^3$ found	$x10^3$ calc.	t	$x10^3$ found	$x10^3$ calc.
No other salt			13.75	8.06	8.09	5.26	5.44	5.46
3.27	1.58	1.58	17.10	9.42	9.42	5.49	5.68	5.68
6.11	3.08	3.08	23.00	11.21	11.22	6.13	6.29	6.28
7.69	3.91	3.88	40.08	13.90	13.98	8.38	8.12	8.16
11.27	5.48	5.53				9.60	9.03	9.04
19.55	8.55	8.52	0.00500 M Cu(NO ₃) ₂			13.44	11.19	11.19
36.32	12.13	12.13	2.21	1.62	1.62	4.06 ^a	8.43	8.48
			3.54	2.70	2.72	11.42 ^a	20.37	20.32
0.0500 M Ba(NO ₃) ₂			5.21	4.09	4.06	0.0200 M Cu(NO ₃) ₂		
3.12	1.53	1.52	7.88	6.04	6.04	1.73	2.52	2.58
7.58	3.87	3.89	11.44	8.22	8.20	2.72	4.04	4.09
13.53	6.58	6.60	15.05	9.92	9.92	3.48	5.28	5.21
21.55	9.22	9.22	19.41	11.47	11.48	4.51	6.62	6.62
33.00	11.72	11.72	0.0100 M Cu(NO ₃) ₂			4.82	7.04	7.02
0.00250 M Cu(NO ₃) ₂			1.19	1.10	1.16	6.33	8.70	8.77
1.84	1.10	1.09	1.44	1.28	1.42	8.30	10.55	10.56
3.78	2.36	2.39	2.79	2.84	2.87	11.77	12.76	12.70
6.47	4.21	4.18	3.50	3.67	3.64	3.30 ^b	4.99	5.26
9.47	5.97	5.98	4.06	4.18	4.24	5.14 ^b	7.38	7.41

^a0.007792 molar ester

^b0.0100 molar HCl

nitrate may therefore be considered as a specific cupric-ion catalysis of reaction 1. As a mean of the values in Table 2, the catalytic constant of cupric ions $k_0'^*$ (cf. equation 3) is found to be 2.69.

Table 2. Bromination of ethyl acetoacetate at 18.0° C in solutions containing 0.002 M HCl, 0.02 M KBr, and C molar barium or cupric nitrate. k^* and h^* are the velocity constants (per minute) of, respectively, reaction 1 and 2.

	C	k^*	h^*	$\frac{k^* - k_0'^*}{C}$
	0	0.01855	0.208	
Barium nitrate	0.0500	0.01897	0.205	0.01
Cupric nitrate	0.00250	0.02538	0.187	2.73
»	»	0.00500	0.03200	0.183
»	»	0.0100	0.04563	0.185
»	»	0.0200	0.07136	0.192

The value of k^* determined here for the solution without added barium or cupric salt is 3 per cent higher than that found in the earlier paper ^{1, 2}. The object of the present examination was more to demonstrate the catalytic effect of the cupric ions than to obtain accurate absolute values of the velocity constants. No effort was therefore made to find the reason for the discrepancy. It is possible that it is connected with the different methods of following the reaction used in the two papers.

THE COMBINED CUPRIC- AND ACETATE-ION CATALYSIS

In order to show that cupric ions catalyse also the proton transfer from ethyl acetoacetate to acetate ions (*cf.* equation 3), measurements were carried out in an acetate buffer solution containing in addition cupric nitrate. Owing to the production of hydrogen ions by reactions 1 and 2 and to the complex formation between cupric and acetate ions, both the cupric and acetate ion concentration change during the reaction. The mathematical analysis of the reaction is therefore very complicated, and it has been necessary to introduce different simplifying approximations.

If we denote the concentrations of ethyl acetoacetate, ethyl monobromoacetoacetate, and ethyl dibromoacetoacetate by, respectively, α , β , and γ , where

$$\alpha + \beta + \gamma = c \quad (5)$$

we have

$$-\frac{d\alpha}{dt} = k\alpha \quad (6)$$

and

$$\frac{d\beta}{dt} = k\alpha - h\beta \quad (7)$$

where k and h are variables given by expression 3 and a similar expression for h . We introduce the approximation that $r = h/k$ is constant. From equation 6 and 7 we obtain

$$\frac{d\beta}{d\alpha} = r \frac{\beta}{\alpha} - 1$$

Integrating and using $\alpha = c$ when $\beta = 0$, we get

$$\frac{\beta}{\alpha} = \frac{1}{r-1} - \frac{1}{r-1} \left(\frac{\alpha}{c}\right)^{r-1} \quad (8)$$

It follows from this equation that, if $r > 2$, $\frac{\beta}{\alpha}$ approaches $\frac{1}{r-1}$ when $\frac{\alpha}{c}$ decreases toward nought, that is, when t increases without limit; and the greater r the more rapid the approach. When r and t are sufficiently great we may use the approximation

$$\frac{\beta}{\alpha} = \frac{1}{r-1} \quad (9)$$

The equivalent concentration of bromine used by the reaction is

$$x = 2\beta + 4\gamma \quad (10)$$

From equations 5, 9, and 10 we obtain

$$c - \frac{x}{4} = \alpha \left[1 + \frac{1}{2(r-1)} \right]$$

Equation 6 may therefore be written as follows

$$-\frac{d\left(c - \frac{x}{4}\right)}{dt} = k \left(c - \frac{x}{4}\right) \quad (11)$$

where k is given by equation 3.

We now introduce the approximation that both the acetate and the cupric ion concentration vary linearly with the concentration of hydrogen bromide formed by the reaction ($= \frac{x}{2}$). We therefore may write

$$c_{\text{Ac}^-} = c_{\text{Ac}^- (\infty)} + p\left(c - \frac{x}{4}\right) \quad (12)$$

and
$$c_{\text{Cu}^{++}} = c_{\text{Cu}^{++} (\infty)} - q\left(c - \frac{x}{4}\right) \quad (13)$$

where
$$p = (c_{\text{Ac}^- (0)} - c_{\text{Ac}^- (\infty)})/c \quad (14)$$

and
$$q = (c_{\text{Cu}^{++} (\infty)} - c_{\text{Cu}^{++} (0)})/c \quad (15)$$

The subscripts (0) and (∞) denote that the concentration corresponds to, respectively, $t = 0$ and $t = \infty$.

It is assumed that the complexes formed between cupric and acetate ions have no catalytic effect (see later). We introduce equations 3, 12, and 13 into equation 11 and use the abbreviations

$$k_{\infty} = k_0 + k'_0 c_{\text{Cu}^{++}(\infty)} + k_{\text{Ac}^-} c_{\text{Ac}^-(\infty)} + k_{\text{Ac}^-'} c_{\text{Cu}^{++}(\infty)} c_{\text{Ac}^-(\infty)} \quad (16)$$

$$l = p[k_{\text{Ac}^-} + k_{\text{Ac}^-'} c_{\text{Cu}^{++}(\infty)}] - q [k'_0 + k_{\text{Ac}^-'} c_{\text{Ac}^-(\infty)}] \quad (17)$$

$$m = pqk_{\text{Ac}^-'} \quad (18)$$

$$n = \sqrt{l^2 + 4k_{\infty}m} \quad (19)$$

We obtain

$$-\frac{d\left(c - \frac{x}{4}\right)}{dt} = \left[k_{\infty} + l\left(c - \frac{x}{4}\right) - m\left(c - \frac{x}{4}\right)^2 \right] \left(c - \frac{x}{4}\right) \quad (20)$$

and, by integration,

$$k_{\infty}^*t = F(x) + I \quad (21)$$

where

$$F(x) = \frac{n+l}{2n} \log \frac{\frac{n-l}{2m} + \left(c - \frac{x}{4}\right)}{\frac{n-l}{2m} + c} + \frac{n-l}{2n} \log \frac{\frac{n+l}{2m} - \left(c - \frac{x}{4}\right)}{\frac{n+l}{2m} - c} - \log \frac{c - \frac{x}{4}}{c} \quad (22)$$

and I is an integration constant.

In the special case when no cupric nitrate is present in the acetate buffer, we have $q = 0$, $l = pk_{\text{Ac}^-}$, and $m = 0$. We therefore obtain by integration of equation 20

$$k_{\infty}^*t = f(x) + I \quad (23)$$

where

$$f(x) = \log \frac{\frac{k_{\infty}}{pk_{\text{Ac}^-}} + \left(c - \frac{x}{4}\right)}{\frac{k_{\infty}}{pk_{\text{Ac}^-}} + c} - \log \frac{c - \frac{x}{4}}{c} \quad (24)$$

Owing to the neglect of the last term of eq. 8, formulae 21 and 23 will hold only when t is sufficiently great. If we plot $F(x)$ or $f(x)$ against t we therefore obtain a curve which, when t increases, more or less rapidly approaches a straight line having the slope k_{∞}^* . In computing k_{∞}^* from a set of experi-

mental data by means of equations 21 and 23, it is necessary to use a method of successive approximations since k_{∞}^* enters into both sides of the equations.

Measurements were first carried out in an acetate buffer without cupric salt. The initial composition of the solution and the experimental data are given in Table 3. The dissociation constant of acetic acid was estimated ⁶

Table 3. Acetate-ion catalysis in the bromination of ethyl acetoacetate at 18.0° C. The solution contained initially 0.003873 *m* ethyl acetoacetate, 0.00974 *M* sodium acetate, 0.100 *M* acetic acid, 0.090 *M* sodium nitrate, and 0.020 *M* potassium bromide. The table shows $f(x)$ computed from the experimental data and, in the last column, $f(x)$ calculated from the linear equation: $f(x) = 0.04022 t - 0.0129$.

t	$(c - \frac{x}{4})10^3$	$f(x)$	$f(x)$ calc.
0	3.873	0.0000	
1.36	3.068	0.0432	0.0418
1.88	2.777	0.0636	0.0627
3.08	2.262	0.1087	0.1110
4.42	1.794	0.1651	0.1649
7.98	1.108	0.3077	0.3081

to be 2.84×10^{-5} . Hence, $c_{\text{Ac}^{-}(o)} = 0.01002$, and $c_{\text{Ac}^{-}(\infty)} = 0.00264$. From equation 14 we obtain $p = 1.905$. Suppose that $k_{\text{Ac}^{-}}^* = 8.21$. From equation 16 and $k_0^* = 0.01855$ we then find $k_{\infty}^* = 0.04022$. $f(x)$ is now computed from the experimental data by means of equation 24. The values obtained are given in the third column of Table 3. When they are plotted against t , all the points fall close to a straight line of the equation given in the text to the table. When $f(x)$ is calculated from this equation the values presented in the last column are found. The slope of the straight line is $k_{\infty}^* = 0.04022$. Hence, we find, in agreement with the supposition, $k_{\text{Ac}^{-}}^* = 8.21$.

Experimental data for the same acetate buffer solution, containing, in addition, 0.00998 molar cupric nitrate, are given in Table 4. From an earlier study ⁶ of the complex formation between cupric and acetate ions, it may be estimated that, for the solution examined,

$$\frac{c_{\text{CuAc}^+}}{c_{\text{Cu}^{++}} c_{\text{Ac}^-}} = 52 \quad \text{and} \quad \frac{c_{\text{CuAc}_2}}{c_{\text{Cu}^{++}} c_{\text{Ac}^-}^2} = 360$$

and that the dissociation constant of acetic acid is 2.84×10^{-5} . Hence, we find $c_{\text{Ac}^{-}(o)} = 0.00720$, $c_{\text{Cu}^{++}(o)} = 0.00717$, $c_{\text{Ac}^{-}(\infty)} = 0.00256$, and $c_{\text{Cu}^{++}(\infty)} = 0.00880$. From equations 14 and 15 we find $p = 1.198$ and $q = 0.421$. Suppose that $k_{\text{Ac}^{-}}'^* = 1143$. Using $k_0^* = 0.01855$, $k_0'^* = 2.69$,

and $k_{Ac^-}^* = 8.21$, we then find from equation 16 that $k_{\infty}^* = 0.0890$, and, from equations 17, 18, and 19, that $l^* = 19.52$, $m^* = 576$, and $n^* = 24.2$. $F(x)$ is now calculated from the experimental data by means of equation 22. The values obtained are given in the third column of Table 4. When they are plotted against t , all the points fall close to a straight line of the equation given

Table 4. Combined acetate- and cupric-ion catalysis in the bromination of ethyl acetoacetate at 18.0° C. The solution contained initially 0.003873 M ethyl acetoacetate, 0.00974 M sodium acetate, 0.100 M acetic acid, 0.00998 M cupric nitrate, 0.0900 M sodium nitrate, and 0.020 M potassium bromide. The table shows $F(x)$ computed from the experimental data and, in the last column, $F(x)$ calculated from the linear equation: $F(x) = 0.0890 t - 0.0220$.

t	$(c - \frac{x}{4})10^3$	$F(x)$	$F(x)$ calc.
0	3.873	0.0000	
1.08	2.908	0.0749	0.0741
1.33	2.690	0.0964	0.0964
1.99	2.189	0.1563	0.1551
2.25	2.046	0.1768	0.1782
3.27	1.538	0.2673	0.2690
4.54	1.095	0.3831	0.3821
7.11	0.591	0.6111	0.6108

in the text to the table. When $F(x)$ is calculated from this equation the values presented in the last column are found. The slope of the straight line is $k_{\infty}^* = 0.0890$. Hence, we find from equation 16, in agreement with the supposition, $k_{Ac^-}^* = 1143$.

DISCUSSION

The results may be summarized in the formula

$$k^* = 0.01855 + 2.69 c_{Cu^{++}} + 8.21 c_{Ac^-} + 1143 c_{Cu^{++}} c_{Ac^-}$$

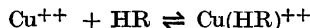
which may also be written in the following way

$$k^* = 0.01855 (1 + 145 c_{Cu^{++}}) + 8.21 (1 + 139 c_{Cu^{++}}) c_{Ac^-}$$

It is seen from the latter expression that cupric ions increase the velocities of both the water reaction and the acetate-ion catalysis by nearly the same factor. The rate-determining step in the base-catalysed bromination of ethyl acetoacetate is considered to be the bimolecular reaction by which a proton is transferred from the ester to the base (*e. g.* water or acetate ion). The cupric ion has no perceptible tendency to take up a proton. It is therefore excluded

that it may act simply as a basic catalyst. We may also exclude the possibility that the effect of cupric nitrate is due to the extremely small concentration of hydroxy-cupric ions ⁷ present in the solution, because it has been shown (see Table 1) that the rate in 0.02 molar cupric nitrate does not change essentially when the concentration of hydrochloric acid is increased from 0.002 to 0.01 molar. The effect of cupric nitrate is too great to be interpreted as a case of a general kinetic salt effect, and its specific character has been demonstrated by the fact that barium nitrate, which is of the same valency type as cupric nitrate, has almost no influence on the velocity (see Table 2). The effect may therefore be classified as a specific cupric-ion catalysis of the proton transfer from the ester to the base. A termolecular mechanism of this reaction is so unlikely that it need not be considered. The rate-determining step is therefore a bimolecular proton transfer, either from the ester molecule to a complex between the base and the cupric ion, or from a complex between the ester and the cupric ion to the base. The former possibility is strongly opposed and the latter supported by the well known experience that, when a base or an acid forms a complex with a cupric ion (or another cation), the strength of the base will highly decrease while that of the acid will greatly increase. The following examples will illustrate this rule. In a study of the complex formation between cupric and acetate ions ⁶, no tendency of the acetato-cupric ion to combine with protons was detectable. For that reason it was also assumed in the present paper, when the rate in solutions containing both acetate and cupric salt was analysed, that acetato-cupric complexes do not catalyse. On the other hand, in a study of the acidity of the hydrated cupric ion ⁷, it was found that the acid strength of the water molecules in this ion is some 10⁷ times as great as that of the free water.

On the basis of these considerations, the following explanation of the cupric-ion catalysis is suggested. It is assumed that the cupric ion and ethyl acetoacetate (HR) in aqueous solution form a complex, and that the equilibrium



is attained practically instantaneously, but only a small fraction of the cupric ions and the ester molecules is transformed into complex ions. When K is the complexity constant we have

$$c_{\text{Cu}(\text{HR})^{++}} = Kc_{\text{Cu}^{++}} c_{\text{HR}}$$

The proton is bound much more loosely, and the ease with which it is given off to a base is much greater, in $\text{Cu}(\text{HR})^{++}$ than in HR. If α_0 denotes

the pseudo-unimolecular, and κ_B the bimolecular velocity constant for the proton transfer from $\text{Cu}(\text{HR})^{++}$ to, respectively, water and a base B, we, therefore, have $\kappa_0 \gg k_0$, and $\kappa_B \gg k_B$. The first order velocity constant for the bromination of ethyl acetoacetate in an aqueous solution containing both cupric ions and a base B may now be written

$$k = k_0 + \kappa_0 K c_{\text{Cu}^{++}} + k_B c_B + \kappa_B K c_{\text{Cu}^{++}} c_B$$

When we, in this equation, set $\kappa_0 K = k'_0$ and $\kappa_B K = k'_B$ we obtain equation 3.

While no other experimental facts indicate the existence of cupric complexes of ethyl acetoacetate, it is known that its (enolic) anion combines with cupric ions in aqueous solution. The stability of the complex formed, and of the cupric compounds of a series of anions of β -diketones, has recently been studied by Calvin and co-workers⁸. Mellor and Maley⁹ have examined similar compounds with other metal ions. There is, however, nothing in these papers that indicates a complex formation between cupric ions and the keto-form of ethyl acetoacetate.

The experimental work reported here was planned only as an introduction to a more careful investigation of the problem including the examination of other metal ions. Owing to the difficulty in obtaining sufficiently accurate velocity constants when consecutive reactions take place, it was decided to continue the investigation with, instead of ethyl acetoacetate, a β -keto-ester having only one α -hydrogen atom, namely 2-carbethoxycyclopentanone, $(\text{CH}_2)_3\text{COCHCOOC}_2\text{H}_5$. A paper dealing with the metal-ion catalysis in the bromination of this ester will soon appear.

SUMMARY

When ethyl acetoacetate reacts with bromine in aqueous solution the two α -hydrogen atoms are replaced by bromine atoms by two consecutive first order reactions which are both catalysed by bases in general. The rate-determining step is, in both changes, a proton transfer from the ester to the base.

In this paper, the effect of cupric nitrate on the rate of bromination in very dilute hydrochloric acid and in acetate buffer has been examined. It was found that cupric ions catalyse the first of the two consecutive reactions (velocity constant k^*) while they have no detectable influence on the second reaction. The results at 18.0° C may be summarized in the formula

$$k^* = 0.01855 + 2.69 c_{\text{Cu}^{++}} + 8.21 c_{\text{Ac}^-} + 1143 c_{\text{Cu}^{++}} c_{\text{Ac}^-}$$

It was also shown that barium nitrate has only an insignificant influence on the rate of bromination in dilute hydrochloric acid.

The effect of cupric ions appears as a catalysis of the proton transfer from the ester to the base (water or acetate ion). In order to explain this catalysis, it is assumed that a small amount of a complex between cupric ions and ethyl acetoacetate is formed. 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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