Addition Compounds of Olefins with Metal Salts

II. The Reaction of Ethylene with Silver Ions in Aqueous Solution

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The reaction between silver ions and ethylene is bimolecular. The reaction is reversible, but the equilibrium is not as strongly displaced towards the reaction product as that of the equilibrium of mercuric ions and ethylene. The former process takes place as a simple addition of ethylene without formation of hydrogen ions.

The equilibrium formation constants were determined at seven temperatures between 17.5°C and 32.5°C. The dependence of the equilibrium constant upon the temperature was determined in 1 M trifluoroacetate solution as:

$$\log_{10} K_1 = -3.42 + \frac{7.37}{2.3 \cdot RT}$$

The relation between the rate constant (time in sec.) and the absolute temperature for the reaction between the aquo silver ion and ethylene in 1 M trifluoroacetate solution was found to be:

$$\log_{10} k_{+1} = 14.88 - \frac{20.36}{2.3 \cdot RT}$$

from determination of the rate constant at five temperatures between 15.0°C and 25.0°C.

In solutions containing triethanolamine(Am) the constants of the following equilibria were determined at 25.0°C:

In contrast to the addition product of ethylene and mercuric ion the corresponding ethylene silver ion was found to be a weak acid (pK about 8.5).

In the present work the reaction between silver ions and ethylene has been studied. The reaction is fast and an equilibrium is established in about 20 min. The equilibrium is obtainable from both sides.

The only silver salt which could be used was the trifluoroacetate. The nitrate and perchlorate ethylene salts turned out to be insoluble. In all experiments a constant salt medium of 1 M sodium trifluoroacetate was used.

Trueblood and Lucas² have shown that only one ethylene molecule combines with the silver ion. In the present work it has been shown manometrically that the reaction is bimolecular with respect to the diaquo silver ion and to ethylene. The following equilibria are assumed:

The equilibrium constants are,

$$K_1 = \frac{[\text{I}]}{[\text{Ag}^+][\text{C}_2\text{H}_4]} \quad (2)$$

and

$$K_2 = \frac{[\text{II}][\text{H}^+]}{[\text{I}]} \quad (3)$$

It has not been possible to prove the existence of an organic form of the ion II:

The results deviate in some respects from those of the corresponding reaction between ethylene and mercuric ions investigated by Brandt and Plum¹. The time of establishing this equilibrium is about 10 h. However, the equilibrium is much more displaced towards the reaction product than that of the silver ion-ethylene reaction.

It is assumed that no measurable amounts of the organic form are formed with silver, while the main product formed with mercury is assumed to be the corresponding organic form. It has been shown that the complex ion I is a weak acid ($\text{p}K = 8.5$), while that of the corresponding mercuric ion is a strong acid ($\text{p}K = -0.5$), but this is understandable as the acidity constants of the corresponding aquo ions differ about 10^8 times.

The equilibrium constant K_1 was determined at seven temperatures in the range from 17.5°C to 32.5°C. The solution was 0.025 M with respect to free hydrogen ions. The dependence of K_1 upon temperature was found to be:

$$\log_{10} K_1 = -3.42 + \frac{7.37}{2.3 \cdot RT} \quad (5)$$

where T is the absolute temperature.

At 25°C, K_1 is 94.0 ± 0.5 . Trueblood and Lucas ² have determined the same equilibrium constant by measuring the partition coefficient of ethylene between silver nitrate solution and carbon tetrachloride, and found the value 85.3.

The acid dissociation constant K_2 of the complex ion I has been determined in solutions containing triethanolamine. In these solutions the following equilibria are assumed together with (1):

where Am stands for triethanolamine. The equilibrium pressure of ethylene was measured together with pH. From these measurements, from the previously found value of K_1 and from the known stoichiometry of the solutions the concentrations of all species of the equilibria could be calculated using the equilibrium constants determined by Bjerrum and Refn ³ for the silver-triethanolamine system.

The values of K_2 and K_3 together with the corresponding values of the concentrations of the ions II and III were calculated by successive approximations. The results are, $K_2 = 2.2 \times 10^{-9}$ and $K_3 = 57.0$ at 25°C.

Finally the value of K_4 was calculated to 2.65 ± 0.15 at 25°C.

The rate constant, k_{+1} , depends upon temperature as,

$$\log_{10} k_{+1} = 14.88 - \frac{20.36}{2.3 \cdot RT} \quad (8)$$

where k_{+1} is measured in mole per liter per sec. and T is the absolute temperature. k_{+1} was determined at five temperatures in the range from 15°C to 25°C. The value at 25°C was found to be, 0.875 mole per liter per sec.

The rate constant, k_{+3} , was determined at one temperature only, 25°C, and found to be, 0.355 mole per liter per sec.

The heat of formation of the ethylene-silver complex was determined as -7.37 kcal/mole as expressed in (5).

The activation energy of $+1$ was found to be 20.36 kcal/mole as shown in (8).

Consequently the energy of activation of -1 is 27.73 kcal/mole.

EXPERIMENTAL

Apparatus. All the experiments were carried out in a Brønsted shaking apparatus similar to that described by Hofman-Bang⁴ and Brandt & Plum¹ with the following alteration: Somewhat larger flasks were used as the consumption of ethylene was much less than obtained with mercuric salts. The total volume of the reaction vessel was usually 175–250 ml.

Materials and solutions. The triethanolamine was of pure grade and was distilled once (bp. 277–279°C at 150 mm Hg). All other chemicals were of analytical grade.

The ethylene was taken from a steel cylinder and purified before being transferred to the apparatus by passing it through six Friedrichs washing bottles, three of which contained concentrated sulphuric acid and three others alkaline pyrogallol solution.

The pure silver perchlorate and trifluoroacetate solutions (only used in preliminary experiments) were prepared by dissolving a known amount of freshly prepared silver oxide in a known amount of free acid in a volumetric flask and diluting with water containing sufficient sodium hydroxide to obtain a total anion concentration of 1.000 mole per liter and a hydrogen ion concentration of 0.025 mole per liter.

In most of the experiments the solutions used were prepared by weighing a known amount of silver nitrate and a known amount of trifluoroacetic acid and diluting with water containing sufficient sodium hydroxide as above. The stoichiometric concentrations of the solutions were: 0.100 silver nitrate; 0.900 trifluoroacetic acid and 0.975 sodium hydroxide which, for the ion concentrations, corresponds to: 0.100 silver ions; 0.025 hydrogen ions and 1.000 for the anions.

The alkaline solutions containing triethanolamine were prepared by weighing the silver nitrate, triethanolamine, trifluoroacetic acid and sodium hydroxide, dissolving each of them in a little water in a volumetric flask; thereafter diluting with water. A survey of these solutions is given in Table 2.

The exact concentration of silver ion was determined by a Volhard titration in the acid solutions, whereas for the alkaline solutions it was calculated from the known amount of silver nitrate weighed.

In the present work, square brackets are used to denote true concentrations, while *C* indicates total concentrations. All the concentrations are in mole per liter, and all pressures are in mm Hg.

The constants given here are therefore not the 'activity constants' but 'concentration constants', valid only under these specific conditions. In the calculation of the constants only concentration in mole per liter are used.

The hydrogen ion concentration, $[H^+]$, was measured with an ordinary glass electrode connected with a 'Radiometer' valve potentiometer, model PHM 3i. $[H^+]$ was determined in every case by standardizing against solutions of well-defined hydrogen ion concentrations having as nearly as possible the same values as the solutions investigated.

Preliminary experiments. Some preliminary experiments were carried out using pure silver nitrate solution, but the solution became opaque within a few minutes and it was impossible to obtain reproducible results. The following values were found for K_1 : 64.7; 67.2; 43.6; 64.2; 77.0 and 84.3.

Other experiments were carried out with a solution of pure silver perchlorate, but the same difficulties occurred again, as a white precipitate was formed within a few minutes. The following values for the equilibrium constant were ascertained: 94.0; 92.1 and 94.2. The average value 92.9 agrees very well with the results obtained in the main experiments (see Table 1), whereas they differ a little from the value found by Trueblood and Lucas².

A few experiments were carried out with other cations, *i. e.*, K^+ and NH_4^+ instead of Na^+ , but in every case a white precipitate occurred within a few minutes.

No precipitation occurs either with pure silver trifluoroacetate solution or with a solution containing 20 % nitrate ions and 80 % trifluoroacetate ions.

The experiments mentioned above were carried out in neutral solution or a solution with a hydrogen ion concentration of 0.025.

Some experiments were carried out in weakly alkaline solutions containing ammonia and ammonium nitrate, ammonium perchlorate or ammonium trifluoroacetate, but a white precipitate occurred in each case. With triethanolamine no precipitation was observed.

Table 1. Results of experiments at various temperatures for determination of the equilibrium constant K_1 in 1 M sodium trifluoroacetate solution. The stoichiometric concentration of the solutions used were:

$C_{\text{AgNO}_3} = 0.1000$, $C_{\text{CF}_3\text{COOH}} = 0.025$ and $C_{\text{CF}_3\text{COONa}} = 0.875$ mole per liter.

Expt. No.	Temperature in °C	K_1	K_1 average	K_1 calculated from (5)
1	17.5	129.1	129.3	129.4
2	17.5	129.4		
3	20.0	114.3	116.1	116.1
4	20.0	118.4		
5	20.0	118.6		
6	20.0	113.1		
7	22.5	100.4	103.4	103.8
8	22.5	103.0		
9	22.5	105.9		
10	22.5	106.0		
11	22.5	101.9		
12	25.0	92.9	94.0	94.0
13	25.0	92.1		
14	25.0	96.3		
15	25.0	95.0		
16	25.0	92.8		
17	25.0	92.3		
18	25.0	93.0		
19	25.0	95.1		
20	25.0	95.0		
21	25.0	96.0		
22	25.0	95.4		
23	25.0	95.3		
24	25.0	92.9		
25	27.5	85.0	84.7	84.7
26	27.5	84.2		
27	27.5	85.0		
28	30.0	74.1	77.2	76.2
29	30.0	76.0		
30	30.0	78.5		
31	30.0	80.2		
32	32.5	68.7	68.5	69.2
33	32.5	68.3		

When employing a great excess of triethanolamine (solution F in Table 2), the uptake of ethylene after 24 h corresponded only to the ethylene dissolved in water. In this solution the concentrations of the monoamine ion and the free silver ion are negligible compared to the concentration of AgAm_2^+ . Thus it is evident that the equilibrium constant K_4 for the reaction between ethylene and the diamine ion, can not be determined directly.

DETERMINATION OF THE EQUILIBRIUM CONSTANTS

The experimental results for the determination of the equilibrium constant K_1 are shown in Table 1. The results are summarized in eqn. (5). Graphical methods were used to obtain the numerical data of the equation.

The concentration of the silver ethylene ion is calculated, using the assumption that the concentration of the ion II is negligible, as being equal to the uptake of ethylene,

$$[I] = \beta(P_0 - P_\infty) - \alpha \cdot P_\infty \quad (9)$$

where P_0 is the initial pressure, P_∞ the pressure of ethylene when equilibrium is established (both expressed in mm Hg), α the molar solubility of ethylene in water at 1 mm Hg pressure, and β an apparatus constant.

As the solubility of ethylene is slight, it may be assumed that Henry's law is valid, and the concentration of free ethylene may therefore be calculated from the equation,

$$[C_2H_4] = \alpha \cdot P \quad (10)$$

where the value of α is 6.34×10^{-6} at 25°C when P is expressed in mm Hg.

Experiment No. 22 in Table 1 may be taken as an example. The volume V of the reaction vessel was 226.4 ml and the volume v of the solution was 100 ml. The value of β is 0.681×10^{-4} . By Volhard titration the initial concentration of the silver ion was found to be 0.0992. The initial pressure P_0 was 258.4 mm Hg and the equilibrium pressure P_∞ was 135.4 mm Hg. From eqn. (12) the value of $[I]$ is calculated to be 0.00752 and the concentration of the free silver ions is thus, $[Ag^+] = 0.0992 - 0.0075 = 0.0917$. The equilibrium constant, K_1 , is,

$$K_1 = \frac{0.00752}{0.0917 \times 6.34 \times 10^{-6} \times 135.4} = 94.4$$

The constancy of the expression of K_1 shows that the assumptions made are reasonable. Perturbations of equilibrium mixtures caused by changes of ethylene pressure lead to reestablishments of equilibrium, independently of the sign of the perturbation.

In order to determine the second equilibrium constant K_2 experiments were carried out in weakly alkaline solutions containing triethanolamine. In Table 2 the compositions of these solutions are stated, and Table 4 gives the results of the absorption of ethylene in these solutions.

From the pH measurements the figures of Table 2 were calculated in the following way. The total amount of triethanolamine, Am, is distributed over the following four species: Am, AmH^+ , $AgAm^+$, and $AgAm_2^+$ each of which can be calculated by means of the following equations,

$$C_{Am} = [Am] + [AmH^+] + [AgAm^+] + 2[AgAm_2^+] \quad (11)$$

$$\bar{n} \cdot C_{Ag^+} = [AgAm^+] + 2[AgAm_2^+] \quad (12)$$

$$[AmH^+] = \frac{[Am][H^+]}{K} \quad (13)$$

Table 2. Solutions containing triethanolamine. The stoichiometric concentrations of the solutions were: $C_{\text{AgNO}_3} = 0.2000$ and $C_{\text{CF}_3\text{COOH}} = 0.800$. In solutions A, B, D and F: $C_{\text{NaOH}} = 0.700$. In solutions C and E: $C_{\text{NaOH}} = 0.780$.

Solution	A	B ₁	B ₂	C	D ₁	D ₂	E ₁ ⁺	E ₂	F
pH (measured)	7.10	8.18	8.40	8.90	7.69	7.83	8.45	8.78	9.20
$\bar{n}$	0.85	1.76	1.79	1.75	1.37	1.41	1.62	1.65	2.00
pAm	2.017	0.791	0.721	0.814	1.395	1.363	1.060	1.015	—
[Am]	0.0096	0.1625	0.1844	0.1533	0.0403	0.0434	0.0912	0.0966	1.81
[AmH ⁺]	0.0626	0.0851	0.0579	0.0153	0.0640	0.0509	0.0263	0.0127	0.09
$\bar{n} \cdot C_{\text{Ag}^+}$	0.1602	0.3524	0.3576	0.3506	0.2740	0.2810	0.3240	0.3304	0.40
$C_{\text{Am}}^{\text{calc.}}$	0.2375	0.6000	0.5998	0.5192	0.3783	0.3753	0.4415	0.4397	2.30
$C_{\text{Am}}^{\text{weighed}}$	0.2380	0.6000	0.6000	0.5200	0.3760	0.3760	0.4400	0.4400	2.30

Bjerrum and Refn³ determined corresponding values of pAm and $\bar{n}$ (the average number of Am molecules bound to one silver ion) in 0.5 M NaClO₄ solution. It is permissible to use these values in our solutions (1 M medium) as the dependence of the equilibrium constants upon the concentration of the inert salt is small as shown by Bjerrum⁶. The value of $\bar{n}$ was found by trial and error.

As an example of the calculations solution D₁ may be used. For the values 1.3 and 1.4 of $\bar{n}$, the C_{Am} is calculated to be 0.3401 and 0.3918, respectively. As it should be 0.3760, the correct value of $\bar{n}$ must be close to 1.4. Using the value 1.37 for $\bar{n}$ we get 0.3783 for the total Am concentration, which is less than 1 % from the correct value.

Ethylene reacts with the silver diaquo ion and with the silver monoamine ion, whereas no measurable reaction takes place between ethylene and the diamine silver ion as proved by the experiments with solution F. The experiments in alkaline solution were carried out at one temperature only, *i.e.*, 25°C.

From the total uptake of ethylene the sum of concentrations of the complex ions I, II, and III can be calculated by means of eqn. (9),

$$C_x = [\text{I}] + [\text{II}] + [\text{III}] \quad (14)$$

The concentration of the ion I is calculated from the expression of K_1 (2). The concentration of the free silver ion is estimated in the following way,

$$C_{\text{Ag}^+} = [\text{Ag}^+] + [\text{AgAm}^+] + [\text{AgAm}_2^+] + C_x \quad (15)$$

denoting $C_{\text{Ag}^+} - C_x = a$ we obtain

$$a = [\text{Ag}^+] + [\text{AgAm}^+] + [\text{AgAm}_2^+] \quad (16)$$

$$[\text{Ag}^+] = \alpha_0 \cdot a; [\text{AgAm}^+] = \alpha_1 \cdot a; [\text{AgAm}_2^+] = \alpha_2 \cdot a \quad (17)$$

where

$$\alpha_0 + \alpha_1 + \alpha_2 = 1 \quad (18)$$

The equilibrium constants for the mono- and diamine silver ions are

$$K'_1 = \frac{[\text{AgAm}^+]}{[\text{Ag}^+][\text{Am}]} = 10^{2.30} \text{ and } K'_{12} = \frac{[\text{AgAm}_2^+]}{[\text{Ag}^+][\text{Am}]^2} = 10^{3.64} \quad (19)$$

From eqns. (16), (17), (18), and (19) we obtain,

$$\alpha_0 = \frac{1}{1 + K'_1[\text{Am}] + K'_{12}[\text{Am}]^2}, \quad \alpha_1 = \frac{K'_1[\text{Am}]}{1 + K'_1[\text{Am}] + K'_{12}[\text{Am}]^2},$$

$$\alpha_2 = \frac{K'_{12}[\text{Am}]^2}{1 + K'_1[\text{Am}] + K'_{12}[\text{Am}]^2} \quad (20)$$

C_x is always a small fraction of the total silver concentration. The ratio C_x/C_{Ag^+} varies between 2 % and 6 %. In the first approximation we can therefore assume that the change of $[\text{Am}]$ caused by uptake of ethylene is negligible. Consequently, approximate values of α_0 , α_1 and α_2 can be evaluated, and knowing $[\text{Ag}^+]$, $[\text{C}_2\text{H}_4]$ and K_1 an approximate value of $[\text{I}]$ is obtained.

$K_2 = \frac{[\text{II}][\text{H}^+]}{[\text{I}]}$ and $K_3 = \frac{[\text{III}]}{[\text{AgAm}^+][\text{C}_2\text{H}_4]}$ are determined by successive approximations. It is assumed that $[\text{II}]$ is small compared to $[\text{III}]$ in solu-

Table 3. Examples of the iteration procedure for the determination of the constants K_2 and K_3 at 25°C. The stoichiometric concentrations of the solutions are given in Table 2.

Solution	Expt.	Values of K_3 calculated from the values of $K_2 \times 10^9 =$			
No.	No.	0	1.6	2.1	2.2
B ₁	35	59.4	58.8	58.5	58.5
B ₂	36	54.8	53.8	53.5	53.4
B ₂	37	58.6	57.6	57.3	57.2
D ₁	41	59.0	58.1	57.7	57.7
D ₁	42	57.4	56.5	56.3	56.2
D ₁	43	56.6	55.6	55.4	55.3
D ₂	44	61.9	60.7	60.3	60.3
D ₂	45	59.1	57.9	57.6	57.5
Average values:		58.3	57.4	57.1	57.0

Solution	Expt.	Values of $K_2 \times 10^9$ calculated on the basis of the value of K_3 :		
No.	No.	58.3	57.4	57.1
C	38	2.1	2.5	2.5
C	39	1.9	2.2	2.3
C	40	1.2	1.6	1.6
E ₁	46	3.1	3.7	3.9
E ₁	47	1.4	2.1	2.3
E ₁	48	0.7	1.3	1.5
E ₁	49	3.0	3.7	3.9
E ₂	50	0.2	0.5	0.6
E ₂	51	1.1	1.4	1.5
Average values:		1.6	2.1	2.2

Table 4. Experiments in alkaline solutions containing triethanolamine at 25°C. P_0 and P_∞ are the initial and equilibrium pressure of ethylene, respectively, in mm Hg. The values of $[\text{Ag}^+]$, $[\text{AgAm}^+]$, $[\text{AgAm}_2^+]$, C_x , [I], [II] and [III] are all to be multiplied by 10^{-4} .

Expt. No.	Solu- tion No.	P_0	P_∞	$[\text{Ag}^+]$	$[\text{AgAm}^+]$	$[\text{AgAm}_2^+]$	C_x	[I]	[II]	[III]	K_4
34	A	217.6	145.2	567.0	1 090.0	228.0	116.0	47.6	12.8	55.5	2.80
35	B ₁	220.1	177.4	13.4	432.5	1 534.0	30.3	1.4	0.5	28.4	2.70
36	B ₂	231.9	207.3	10.6	390.0	1 569.4	29.4	1.3	0.7	27.3	2.44
37	B ₂	229.2	203.9	10.6	390.0	1 569.4	30.8	1.3	0.7	28.8	2.62
38	C	219.1	191.1	14.7	450.9	1 494.7	36.3	1.7	2.8	31.8	2.69
39	C	219.5	191.6	14.7	450.9	1 494.7	36.1	1.7	2.8	31.6	2.59
40	C	221.7	194.0	14.7	450.9	1 494.7	35.6	1.7	2.9	31.0	2.58
41	D ₁	225.7	175.6	120.0	960.0	840.0	75.5	13.0	1.4	61.2	2.62
42	D ₁	221.3	174.2	120.0	960.0	840.0	73.2	12.9	1.3	59.0	2.55
43	D ₁	216.3	172.8	120.0	960.0	840.0	71.7	12.7	1.3	57.6	2.51
44	D ₂	214.1	163.8	114.0	987.0	830.0	75.6	11.6	1.6	62.4	(2.97)
45	D ₂	225.1	174.5	114.0	987.0	830.0	76.4	12.3	1.7	62.4	2.77
46	E ₁	204.1	172.4	36.0	652.0	1 262.0	48.3	3.8	2.1	42.4	2.79
47	E ₁	200.6	170.6	36.0	652.0	1 262.0	46.1	3.7	2.1	40.3	2.67
48	E ₁	206.7	175.7	36.0	652.0	1 262.0	46.7	3.8	2.2	40.7	2.62
49	E ₁	201.5	170.0	36.0	652.0	1 262.0	47.6	3.7	2.1	41.8	2.78
50	E ₂	226.7	191.6	32.5	626.0	1 291.7	48.5	3.8	2.2	42.5	2.60
51	E ₂	245.7	206.6	32.5	626.0	1 291.7	54.5	4.1	2.3	48.1	2.73

tions B and D. This gives a rough determination of K_3 . From this value of the constant, [III] is calculated for solutions C and E and estimate is obtained for the concentration [II] and the constant K_2 . Using this value of K_2 , [II] is calculated in solution B and D and the assumption that [II] is small compared to [III] is seen to be justified. The concentration [III] and K_3 are now adjusted by aid of the correction, and new values of [II] and K_2 are obtained. After a few iterations K_2 and K_3 became really constant.

In Table 3 examples of the iteration procedure are given. From K_3 and the equilibrium constants of Bjerrum and Refn³ (19) K_4 could be calculated. The values for K_4 are shown in Table 4. The small calculated value, 2.65, is in agreement with the experimental fact that solutions in which the ion AgAm_2^+ is predominating do not take up ethylene.

MEASUREMENT OF THE RATE OF REACTION WITH THE SILVER AQUEOUS ION

In Table 6 a representative run is shown. It is seen that it takes about one minute before stationarity is established between the rate of solution of ethylene and the velocity of the reaction with silver ions. In this first minute, there is not enough ethylene in the solution (even though the solubility rate

is very high), as the rate of reaction is very great. Then for about 2 min the reaction takes place at a rate that permits of measuring the pressure exactly at the desired time. The rate constant in this interval is almost a true constant. In the first minute nearly 70 % of the complex is formed, and in the following 2 min about 26 %. After about 20 min the equilibrium is established, and in this last interval the remaining 4 % of the complex is formed.

The calculation of the rate constant, on the basis of the assumption that the reaction is bimolecular, is made by means of the equation:

$$-\frac{d[\text{C}_2\text{H}_4]}{dt} = k_{+1}[\text{Ag}^+][\text{C}_2\text{H}_4] - k_{-1}[\text{Ag}(\text{C}_2\text{H}_4)^+] \quad (26)$$

The integrated form of this equation is:

$$\frac{K \cdot P_\infty}{P_0 - 2P_\infty - K\alpha^2 P_\infty^2 \log e} \log \frac{K\alpha P_\infty(P_0 - P) - (P_0 - P_\infty)}{K\alpha P_\infty(P_0 - 2P_\infty) + P_\infty} = k_{+1} \cdot t \quad (27)$$

$$\text{where } K = \frac{\alpha \cdot P_\infty - \beta(P_0 - P_\infty)}{\alpha \cdot P_\infty(\alpha \cdot P_\infty + \beta(P_0 - P_\infty) - C_{\text{Ag}^+})} \quad (28)$$

As a rule the rate constant was determined from the slope of the straight line plot of logarithmic expression (27) against t , usually simplified to:

$$\frac{K}{\sqrt{q} \cdot \log e} \log \frac{x + A}{x + B} = k_{+1} \cdot t \quad (29)$$

where: $a = K \cdot \alpha \cdot P_0 \cdot C_{\text{Ag}^+}$; $b = -1 - c \cdot C_{\text{Ag}^+} - \frac{a}{C_{\text{Ag}^+}}$;

$$c = \frac{K\alpha(P_0 - P_\infty)}{C_x} ; \quad q = b^2 - 4ac ; \quad A = \frac{b - \sqrt{q}}{2c} ;$$

$$B = \frac{b + \sqrt{q}}{2c} \text{ and } x = \frac{C_x(P_0 - P)}{P_0 - P_\infty}$$

(x is the concentration of the complex ion at the time t).

In all the tables in this paper the rate constants are given in mole per liter per min.

As small amounts of atmospheric air are always present in ethylene, the concentration of the air was determined by reaction with a mercuric salt solution and a deficit of ethylene. The value of the pressure when equilibrium had been established was used to calculate how much atmospheric nitrogen was mixed with the ethylene (the oxygen was absorbed in the basic pyrogallol before the ethylene was transferred into the reaction chamber). Usually the nitrogen content was about 3–5 %.

Some experiments were carried out in the opposite direction, by starting with a solution in equilibrium with ethylene at high pressure. By decreasing the pressure with about 200 mm Hg, a reaction occurs in the reverse direction, as ethylene is now given off. In Table 7 the calculation of one of these

Table 5. Results of experiments for determination at various temperatures of the rate constant in 1 M trifluoroacetate solution of the reaction between silver diaqueous ions and ethylene. The stoichiometric concentrations of the solution are the same as described in Table 1.

Expt. No.	Tempe- rature in °C	k_{+1}	k_{+1}	k_{+1}	forward (ordinary) or reciprocal
			average	calculated	
52	15.0	16.2	16.2	15.9	o
53	17.5	18.4	21.6	21.7	r
54	17.5	23.5			r
55	17.5	22.1			r
56	17.5	22.6			r
57	20.0	29.2	29.2	29.2	o
58	20.0	27.6			r
59	20.0	29.5			r
60	20.0	30.4			r
61	20.0	29.0			o
62	22.5	37.3	39.1	39.4	o
63	22.5	38.9			o
64	22.5	32.0			r
65	22.5	43.7			o
66	22.5	37.1			r
67	22.5	45.1			r
68	25.0	52.9	52.7	52.5	o
69	25.0	52.9			r
70	25.0	49.0			o
71	25.0	53.1			r
72	25.0	49.5			o
73	25.0	53.4			r
74	25.0	54.6			o
75	25.0	50.4			r
76	25.0	53.2			o
77	25.0	55.2			r
78	25.0	56.2			o
79	25.0	50.9			r
80	25.0	52.5			o

experiments is shown, and it is seen that the pressure increases about 50 mm Hg in the first 3 min, and only 2 mm Hg in the following 20 min, thereafter the equilibrium is again established.

The calculation is carried out by means of the same equation as above (26), but as the initial concentration of the complex ion is not at zero, the integrated expression differs slightly from eqn (27):

$$\frac{K}{\sqrt{q} \cdot \log e} \left(\log \frac{y + A}{y + B} - \log \frac{y_0 + A}{y_0 + B} \right) = k_{+1} \cdot t \quad (30)$$

Table 6. Measurement and calculation of an ordinary experiment. This experiment is the same as No. 68 in Table 5. $V = 226.4$ ml; $v = 100$ ml; $\beta = 0.681 \times 10^{-4}$; $a = 5.96$; $b = -2.122$; $c = 9.76$; $\sqrt{q} = 1.978$; $A = -0.210$; $B = -0.0075$.

Time in min	P ; $\log \frac{x+A}{x+B}$	$-\log \frac{A}{B}$; $k_{+1} = \frac{K_1}{\sqrt{q} \cdot \log e} \cdot \frac{\log \frac{x+A}{x+B} - \log \frac{A}{B}}{t}$
0.00	260.6	0.000
0.25	224.6	0.114
0.50	203.6	0.232
0.75	187.6	0.350
1.00	173.6	0.490
1.25	165.1	0.606
1.50	159.6	0.701
1.75	154.0	0.832
2.00	150.5	0.968
2.25	148.1	1.031
2.50	145.4	1.159
2.75	143.7	1.284
3.00	142.6	1.356
5.00	138.8	1.972
20.00	137.8	(43.2)

where y_0 is the initial concentration of the complex ion and y its concentration at time t . The expressions for b , q , A and B are the same as above, while a and c are:

$$a = K \cdot \alpha \cdot P \cdot C_{Ag^+} + c \cdot y_0 \cdot C_{Ag^+}; \quad c = \frac{K \cdot \alpha (P_{\infty} - P_0)}{y_0 - y_{\infty}}$$

A summary of the results of the experiments is given in Table 5 (in the last column an 'o' or 'r' indicate whether the experiment is a forward or a

Table 7. Measurement and calculation of the reciprocal reaction. This experiment is the same as No. 71 in Table 5. $V = 226.4$ ml; $v = 100$ ml; $\beta = 0.681 \times 10^{-4}$; $a = 0.0177$; $b = -1.899$; $c = 7.26$; $\sqrt{q} = 1.758$; $A = -0.2510$; $B = -0.0097$.

Time in min	P ; $\log \frac{y+A}{y+B}$	$-\log \frac{y_0+A}{y_0+B}$; $k_{+1} = \frac{K_1}{\sqrt{q} \cdot \log e} \cdot \frac{\log \frac{y+A}{y+B} - \log \frac{y_0+A}{y_0+B}}{t}$
0.00	129.1	0.000
0.50	152.1	0.251
1.00	164.6	0.479
1.17	168.0	0.572
1.33	170.0	0.646
1.50	171.0	0.673
1.67	172.9	0.751
1.83	175.0	0.860
2.00	175.6	1.005
2.50	177.9	1.090
3.00	179.0	1.195
5.00	179.9	1.320
20.00	180.9	(32.4)

reciprocal reaction). Employing Arrhenius' equation in 1 M trifluoroacetate solution all the results are expressed as follows:

$$\log_{10} k_{+1} = \log_{10} A - \frac{E_A}{2.2 \cdot RT} = 14.88 - \frac{20.36}{2.3 \cdot RT} \quad (31)$$

The value of the energy of activation (expressed in kcal) and the value of the frequency exponent are in good agreement with other values found in rapid complex reactions⁵. The value of the rate constant given in the last column is calculated from this equation and is in very good conformity with the experimental average value.

The value of the rate constant in dilute aqueous solution must be of the same order of magnitude as the one found in 1 M salt solution, because the reaction occurs between an ion and a neutral molecule. From the equation:

$$\log K_1 = \log \frac{k_{+1}}{k_{-1}} \quad (32)$$

the dissociation velocity constant k_{-1} for the mono ethylene complex silver ion can be calculated, and from the equation:

$$Q = E_A - E_{-A} \quad (33)$$

the energy of activation for the dissociation reaction of the complex ion can also be calculated; the value of E_{-A} is found to be 27.73 kcal.

MEASUREMENT OF THE RATE OF REACTION WITH SILVER TRIETHANOLAMINE ION

In Table 8 a survey is given of the results for determination of the rate constant for the reaction between the silver triethanolamine ion and ethylene (5). The value found is about half of that found for the aquo ion, *i.e.*, it is of the same order of magnitude as for the aqueous ion.

As previously mentioned the hydrogen ion concentration is the same before and after reaction with ethylene. As not more than about 2 % of the total

Table 8. Results of experiments for determination of the rate constant at 25°C for the reaction between the silver mono triethanolamine ion and ethylene.

Expt.No.	Solution	k_{+1}	$k_{+1}(\text{average})$
81	B ₁	21.3	
82	B ₁	21.4	
83	B ₁	21.0	21.3
84	B ₁	22.1	
85	C	20.5	

amount of silver ions reacts with ethylene, the calculation of these experiments can be made using the assumption that the free silver ion concentration as well as the concentration of the mono triethanolamine silver ion are both

constant, i.e., $\bar{n}$ is constant. As the concentration of the ion I is only about 5 % of the total amount of the complex ions formed, the calculation can be made under the assumption that a reaction with ethylene occurs only with the mono triethanolamine silver ion. Eqn. (27) can therefore be simplified to:

$$\frac{\beta(P_0 - P_\infty) - a \cdot P_\infty}{a \cdot a \cdot P_0 \cdot \log e} \log \frac{P_0 - P}{P_0 - P_\infty} = k_{+1} \cdot t \quad (34)$$

where 'a' is the concentration of the silver mono triethanolamine ion.

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