

Kinetics and Mechanism of Acetylene Hydrochlorination Catalyzed by Cuprous Complexes in Solution

III.* Catalyst Solution in Equilibrium with Solid Cuprous Chloride. Accurate Determination of the Initial Value of a Kinetic Function

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Our preceding tentative experiments indicate that the formation of vinyl chloride in a catalyst consisting of hydrochloric acid and cuprous chloride is of first order in acetylene, if the solution is in equilibrium with solid cuprous chloride during the reaction.

At further testing of this hypothesis it has proved advantageous to let acetylene be represented in the kinetic formulae by its total concentration in the liquid phase A_d instead of by its partial pressure P_A . A tentative analysis of the rate function

$$\frac{dB}{dt} = F_{sc}(HCl_t, A_d)$$

is accomplished in the following steps:

a) For every reading belonging to the pressure time curve of the very accurate manometrical experiment we compute the quantity

$$\kappa_c = \frac{1}{t} \int_0^t \frac{dB}{A_d}$$

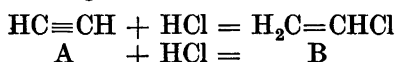
which constitutes the time mean of the quotient $f_c = F_{sc}/A_d$. The reaction is approximately of the first order. The quantity κ_c shows, however, a decreasing trend of 4-6 % during the conversion — thus f_c decreases too. A decrease can be predicted due to the consumption of HCl and it is necessary to take this effect into consideration although the HCl_t dependence of the reaction velocity is unknown.

b) The κ_c^0 -value corresponding to the initial value HCl_t^0 is determined by graphical extrapolation and is a good approximation of the f_c -value. The values are independent of A_d judging from a series of experiments with the same HCl_t^0 .

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Special attention has been directed to such numerical and algebraic problems that regularly appear in the treatment of accurate velocity data from nearly monomolecular reactions. Thus a suitable way to determine numerically the integral which enters into κ_c is pointed out as well as a special method to determine κ_c^0 by extrapolation. An end value problem occurs: the directly measured P_∞ value is biased by a slow reaction which does not effect the P values of the main period. We have solved the problem by means of a hypothetical correction which can be checked at a later stage.

It is clear from the preceding papers in this series that the hydrochlorination of acetylene according to



takes place in aqueous solutions of cuprous chloride complexes with good yield at 25°C. The reaction can be considered quantitative within quite wide limits of the reaction conditions. It is a homogeneous catalytic reaction, even if solid Cu^{I} -compounds are present. The velocity is independent of concentration (and partial pressure) of formed vinyl chloride. The course of the reaction can be followed in a closed system by a manometrical technique which gives velocity data of unusually high accuracy provided some difficulties arising from diffusion resistance, non ideal compressibility etc. are avoided. The conversion degree Y , the acetylene partial pressure P_A and other quantities required for a kinetic analysis are computed from the time pressure curve with an accuracy that corresponds well to the accuracy of the primary readings.

The tentative experiments have been of two different types:

(a) Catalyst solution with constant total concentration of dissolved cuprous chloride.

(b) Catalyst solution with constant cuprous chloride activity, maintained by presence of solid cuprous chloride.

In both cases the time-pressure curve is monomolecular in the first approximation, which corresponds to an approximately first order reaction in acetylene. In the (a)-experiments, however, a more precise treatment shows an obvious systematic deviation.

In Part I and II the treatment of the (b)-experiments was directed on an analysis of the relation:

$$\frac{dB}{dt} = F_s(\text{HCl}_t, P_A) \quad (1)$$

where B stands for formed amount of vinyl chloride (per unit amount of catalyst or catalyst-component) and where the hydrogen chloride concentration HCl_t and acetylene partial pressure P_A appear as independent variables.

The experiments in Part II indicate that the reaction is of exactly first order in P_A , *i.e.* that the function F_s has such form that the quotient

$$f_p \equiv \frac{F_s(\text{HCl}_t, P_A)}{P_A} \quad (2)$$

is a function of HCl_t only.

It was natural to direct further investigations on this hypothesis in order to confirm that the f_p -quantity is independent of P_A under other conditions as well regarding HCl_t and other components, and to study the functional relation between f_p and HCl_t .

In the next paragraph a change of variables has been performed. This has caused an alteration of the aim — merely formal, however.

SYMBOLS

- n_t Added amount of acetylene. Unit: mmoles.
 A Remaining acetylene in mole per unit amount of catalyst.
 Unit: $m = \text{mole}/1000 \text{ g H}_2\text{O}$.
 A_d Dissolved acetylene. Unit: m .
 B Formed vinyl chloride per unit amount of catalyst. Unit: m .
 φ_A Total acetylene capacity of the system, mole/pressure unit and unit amount of catalyst. Unit: $m \cdot \text{atm}^{-1}$ (or $m \cdot \text{mm}^{-1}$).
 φ_B Total vinyl chloride capacity. Unit: $m \cdot \text{atm}^{-1}$.
 φ_g Capacity of gas phase, for ideal gas. Unit: $m \cdot \text{atm}^{-1}$.
 Φ_g Absolute capacity of gas phase, for ideal gas. Unit: $\text{mole} \cdot \text{mm}^{-1}$.
 α_A Absorption coefficient of acetylene. Unit: $m \cdot \text{atm}^{-1}$.
 P "Dry" total pressure, $P_{\text{tot}} - P_v$. Unit: atm or mm Hg uncorr.
 (= 760.7^{-1} atm). P_v = vapour pressure of catalyst solution.
 Special kinetic functions:

$$f_p = \frac{1}{P_A} \cdot \frac{dB}{dt}; \quad f_c = \frac{1}{A_d} \cdot \frac{dB}{dt}$$

$$I_c = \int_0^Y \frac{A_{00} \cdot dY}{A_d}; \quad k_c = (I_c - I_c^0)/t$$

Index $_0$ of P_0 , HCl_t^0 , I^0 , f_c^0 etc. marks value at $t = 0$. P_{00} stands for the equilibrium pressure which corresponds to the acetylene amount A_{00} and P_∞ stands for the end pressure, directly measured ($P_{\infty m}$) or calculated ($P_{\infty c}$). The following normalized kinetic variables are used:

$$Y_p = (P - P_{00}) / (P_\infty - P_{00})$$

$$Y = B/A_{00}, \text{ conversion degree}$$

$$Z = 1 + Y/\ln(1 - Y)$$

Constants: $\gamma = 0.0759 \text{ atm}^{-1}$, defined in (5); γ' defined in (14); ξ correction factor according to (8); ψ defined in (10);

TOTAL CONCENTRATION OF ACETYLENE — A_d — AS A PRIMARY KINETIC VARIABLE

It has proved advantageous to use the quantity $A_d = [C_2H_2]_t$, i.e. the total concentration of dissolved acetylene as a primary kinetic variable instead of P_A . The aim of the measurements then changes into an empirical determination of the function

$$\frac{dB}{dt} = F_{sc}(HCl_t, A_d) \quad (3)$$

It can be supposed that the reaction is of first order in A_d too, *i.e.* that the quotient f_c , defined by

$$f_c \equiv \frac{F_{sc}(HCl_t, A_d)}{A_d} \quad (4)$$

will turn out to be a pure HCl_t -function, independent of A_d . The reason is that the concentration of dissolved acetylene is nearly proportional to P_A . According to the general formula which was put up on the basis of previous investigations:^{1,2}

$$A_d = \alpha_w P_A + \beta\{CuCl\}P_A + \gamma\{CuCl\}HCl_t P_A \quad (5)$$

the premises "CuCl(s) and HCl_t constant" are sufficient for a proportionality between A_d and P_A . The formula has a limited validity; in the dependence of HCl_t there is an appreciable deviation approaching some percent in the interval $7 < HCl_t < 10$ m. But the proportionality between A_d and P_A holds with a higher accuracy. In our earlier measurements there is no deviation from the relation

$$A_d = P_A \cdot \alpha_A \quad (6)$$

(where α_A is a function of HCl_t only) exceeding 0.5 % in the interval $0.1 < P_A < 1.2$ atm. Due to non ideal compressibility, deviations of this size can be expected — as can be seen in Part I.

From (6) and the definitions $f_p = P_A^{-1} \cdot dB/dt$ and $f_c = A_d^{-1} \cdot dB/dt$ follows the relation:

$$f_p = \alpha_A \cdot f_c \quad (7)$$

It is thus clear that if f_p is nearly independent of P_A , then f_c is also nearly independent of A_d . There is *a priori* no reason to assume that a possible small difference in the degree of independence should be to the benefit of f_p .

This might create the impression that A_d or P_A may be used arbitrarily as variable. But the use of A_d has been of value for several reasons, first of all because a simple empirical function $f_c(HCl_t)$ is eventually established. The quantity f_c also grows less rapidly with HCl_t ; thereby we avoid several inconveniences, occurring in the examination of the relation between f_p and HCl_t . It is also important that f_c is negligibly influenced by that error in the ϕ_A -value, which derives from the "reaction free" equilibrium pressure P_{00} . Determination of P_{00} in these experiments involves special difficulties (see Part I) and the error is quite dominating at the direct determination of f_p . Hence it is better to compute f_p — of interest as well — as $\alpha_A \cdot f_c$ according to (7) using a smoothed α_A -function, based on special measurements with a suitable experimental technique. We thus avoid the less accurate α_A -value which is calculated from the P_{00} -value of the individual kinetic experiment.

Here of course we consider A_d as a purely empirical variable chosen because it is a suitable and directly determinable quantity which — together with

HCl_t — gives an unambiguous description of the system. But the choice of A_d as variable does not at all express a guess that all species in the solution containing acetylene should react equally fast, such an assumption being very improbable.

COMPUTATION OF THE END PRESSURE P_∞ AND OTHER NECESSARY CONSTANTS

For the computation of the conversion degree Y , the quantity A_d , etc. we need — besides the pairs of values of the time pressure curve — some other quantities which are characteristic constants for every individual experiment. The start pressure P_0 is determined by extrapolation regarding the initial deviation caused by the acetylene absorption. To increase the accuracy of the P_0 -value we use a whole series of readings — the “start period” — which has been reserved for this purpose. Cf. Part I, where the P_0 -determination is treated in detail. Also the constants P_{00} = the “reaction free” equilibrium pressure and ϕg = the gas phase capacity are determined by methods described in Part I. Only for the end pressure P_∞ a new procedure has been developed.

The pressure fall of the end period. If the end period is long enough we observe a slow pressure fall with constant velocity of the magnitude 0.005—0.5 mm/h — see Fig. 1. The same phenomenon appears at the calibration with vinyl chloride, when the reaction flask contains pure vinyl chloride added in substance. We have not studied the phenomenon closely but the lubrication of stopcocks and joints is probably of importance. This is supported by the fact that experiments with fluorohydrocarbon greasing show considerably slower pressure fall than the others with silicon grease.

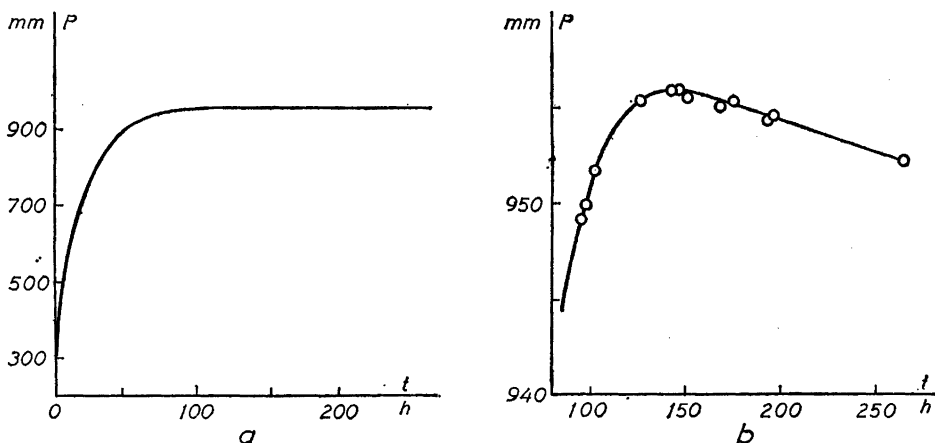


Fig. 1. Pressure time curve from experiment 6. a: The entire experiment. b: The end period (98.7—100.0% conversion) in enlarged scale.

Anyhow, the phenomenon has nothing to do with the main reaction and cannot either — whichever reasonable assumption we make about its cause and kinetics — bias the pressure values belonging to the main period of the experiment; only the end pressure P_∞ is in error.

A general remark on the end value problem in kinetic investigations. When testing a kinetic formula on observed data of X and t it is often necessary to know the end value of X_∞ of the measured variable. A common case is that the remaining concentration of a reactant is proportional to the difference $|X - X_\infty|$. For a direct determination of X_∞ the measurements must be extended over a considerable period of time, especially if the demand for accuracy is high. At a dispersion of $\sigma(X) = \pm 0.1$ and a total interval of $|X_0 - X_\infty| = 500$ — which is the level of accuracy that our experiments approach — 13 half times (first order reaction presumed) would be necessary to make the difference between X and X_∞ less than $\sigma(X)$. Then it is probable that disturbances occur making the X_∞ -value much less reliable than the bulk of the measured values.

If it is known that the reaction is exactly of first order the difficulty can be avoided for in principle the readings from the main period (3 or at most 4 half times) are sufficient also for the determination of the constant X_∞ . To facilitate the calculations Guggenheim's method³ can be used provided the readings are made according to a certain time schedule. But the problem can be solved also without such tricks being nothing but a numerical difficulty. Suitable statistical methods⁴ have been known for a long time. But if the kinetic relation is quite or partly unknown and must be determined by testing different alternatives it is hardly possible to get on without a measured X_∞ value.

In our case it has been possible to solve the problem with the aid of a *hypothetical correction*. By observations at a very late stage where the main reaction certainly has ceased we collect information on the disturbance which is the cause that no constant end value of X is obtained. We regard the disturbance formally as a vinyl chloride reaction and make a reasonable assumption about its kinetics. According to this we compute corrections for the readings of the end period and the result will be a constant value which is accepted as X_∞ .

Our intention is to check the hypothesis later on as soon as we have found an applicable kinetic relation by means of graphical methods using the adjusted X_∞ -value. The accepted relation will eventually be used in a statistical treatment where the best value for the constant X_∞ is determined, using unadjusted values of the main period only.

Correction for vinyl chloride loss. If the reaction flask contains vinyl chloride only the velocity of the pressure fall is approximately proportional to the pressure (at unchanged greasing). We now assume that nothing but vinyl chloride disappears and that the loss is proportional to the partial pressure P_B also during the main period. If P_B is set proportional to the difference $(P - P_0)$ the following expression for the accumulated loss, measured in pressure, is found

$$P_D = \xi \int (P - P_0) dt \quad (8)$$

The integral is determined by graphic integration (with moderate accuracy) of the original time pressure curve $(P - P_0) \sim t$ thus avoiding such kinetic constants that are not computed until a later stage of the calculation. The correction factor ξ can easily

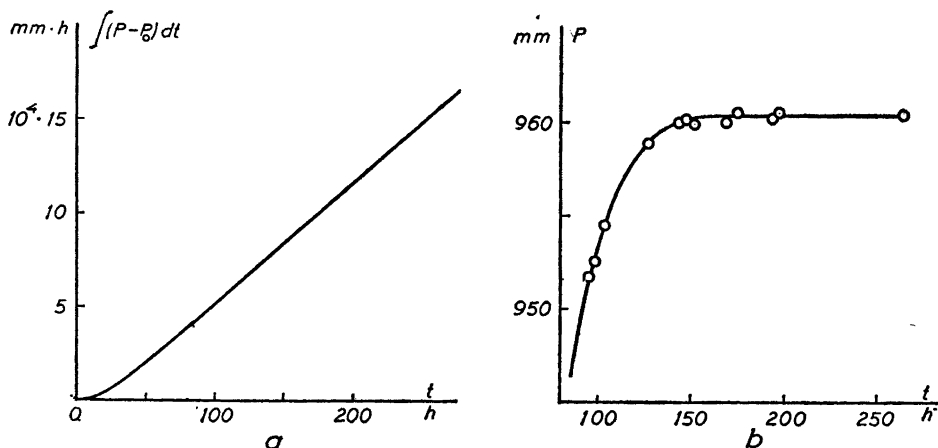


Fig. 2. Correction for vinyl chloride loss. Experiment 6. *a*: The result of graphic integration of the $P-t$ -curve in Fig. 1 *a*. *b*: Corrected end course; $P_{\infty} = 960.4$.

be calculated from the constant pressure fall during the end period, *i.e.* when P in the integral can be set approximately constant.

Expt. 6 makes a good example of this adjustment. In Fig. 1 is found in part *a* a survey of the entire $P-t$ -course of the experiment and in part *b* a curve showing the end period in enlarged scale. The curve approaches a falling straight line whose slope corresponds to 0.034 mm/h , giving the correction factor $\xi = 5.2 \times 10^{-6} \text{ h}^{-1}$. Fig. 2 *a* shows the integral curve which is used. It can be seen from the figure that the integral during the end period approaches a linear function so the adjustment ΔP_D for readings with $t > 80$ h can be computed according to $\Delta P_D = 0.034 (t - 20)$.

Fig. 2 *b* shows the adjusted end course; the values approach the constant end pressure $P_{\infty} = 960.4$ which lies about 4 mm higher than the uncorrected maximum pressure. For the last readings during the main period (5–13 h) we find small corrections which can be abbreviated to $+ 0.1 \text{ mm}$ for all.

Similar corrections are made in most experiments with correction factors computed either from the pressure fall in the experiment's own end period or at the vinyl chloride calibration. In some cases the corrections become very small and quite uncertain so we have neglected them.

Comparison between end pressures, computed in different ways. The calibration with pure vinyl chloride which is made in connection with the experiment has the purpose to determine the theoretical end pressure P_{∞} . The procedure has been described more in detail in Part I. In Table 1 this value is compared with $P_{\infty m}$ from the adjusted end period; the unadjusted vertex P_{\max} of the time pressure curve is also given. For the relative difference between $P_{\infty m}$ and P_{∞} is stated only that error which is due to the uncertainty in P_{∞} .

The yield of the reaction. In the calculation of the yield it is assumed that only soluble byproducts are formed. As can be seen from Table 1 the yield values are excellent in 8 m HCl and higher, but at low HCl_t a significant deviation appears, probably due to the formation of acetaldehyde. (The table includes data from all experiments even those which are presented in the next paper in this series.)

Table 1. Computed and measured end pressures; yield of the reaction.

HCl_t m	Expt. No.	P_{\max} mm	$P_{\infty m}$ mm	$P_{\infty c}$ mm	Diff ($P_{\infty m} - P_{\infty c}$) %	Yield %
5.53	9	621.8	622.1	670.8 ± 1.3	-7.25 ± 0.22	92.7 ± 0.2
6.50	10	874.1	881.1	897.1 ± 1.7	-1.78 ± 0.21	98.2 ± 0.2
7.25	11	1025.4	1032.4	1035.1 ± 1.8	-0.26 ± 0.19	99.7 ± 0.2
7.94	7	908.1	910.0	908.0 ± 2.1	+0.22 ± 0.25	100.2 ± 0.2
8.57	12	1105.1	1111.1	1113.2 ± 2.1	-0.19 ± 0.21	99.8 ± 0.2
9.05	5	534.9	536.0	537.8 ± 1.4	-0.33 ± 0.30	99.7 ± 0.3
9.06	6	955.9	960.4	957.5 ± 1.7	+0.30 ± 0.20	100.3 ± 0.2
9.05	13	—	—	1416.2 ± 2.5	—	—
9.10	14	1006.6	1012.2	1014.5 ± 2.8	-0.23 ± 0.30	99.8 ± 0.3
10.05	15	1093.5	1098.8	1097.1 ± 2.5	+0.16 ± 0.25	100.2 ± 0.3

THE QUANTITY κ_c AND ITS DEPENDENCE ON THE CONVERSION DEGREE

Algebraic and numerical treatment. In the computation of the quantity

$$\kappa_c \equiv \frac{1}{t} \int_0^B \frac{dB}{A_d} \quad (9)$$

it has turned out to be suitable to choose the conversion degree $Y = B/A_{00}$ as integration variable. We then follow the general rule presented in Part II, p. 1234, which implies that the integration can be made exact and that the approximation, allowed in the $Y-P$ relation, can be checked.

For the computation of Y from the read P -values (and constants) we use the expression

$$Y = \frac{Y_p}{1 + \psi(1 - Y_p)}$$

where

$$Y_p = (P - P_{00}) / (P_{\infty} - P_{00}) \quad (10)$$

and

$$\psi = \gamma P_{00}^2 / (P_{\infty} - P_{00})$$

occurring already in Part II. The inherent approximation can be checked with the more exact formulae (I-30) which show that the Y -error is less than the error derived from the reading uncertainty in P . In the κ_c -expression (9) the differential $dB = A_{00} \cdot dY$ can be introduced, as is evident from the definition of Y . It then remains to express the quotient A_{00}/A_d as a Y function.

As A_d is the dissolved part of the total acetylene amount A we can apply the general relation

$$\frac{A_d}{A} = \frac{\varphi_A - \varphi_g}{\varphi_A} \quad (11)$$

Since $A = A_{00}(1 - Y)$ we get

$$\frac{A_{00}}{A_d} = \frac{\varphi_A}{\varphi_A - \varphi_g} \cdot \frac{1}{1 - Y} \quad (12)$$

which is also a general relation, valid even if the φ -quantities are considered as variables. We apply to φ_A the relation which according to Part I holds at the conditions “{CuCl} constant and $HCl_t = HCl_t^0 - B$ ”, viz.

$$\varphi_A = \frac{A_{00}}{P_{00}} - \gamma \cdot B \quad (13)$$

If (13) is substituted in (12) we get after a subdivision in partial fractions and simplification:

$$\left\{ \begin{array}{l} \text{where} \\ \frac{A_{00}}{A_d} = a_1(1-Y)^{-1} - b_1(1-\gamma'Y)^{-1} \\ a_1 = \frac{A_{00}}{A_{00} - \varphi_g P_{00}} \left(1 + \frac{\varphi_g P_{00}}{A_{00}} \cdot \frac{\gamma'}{1-\gamma'} \right) \\ b_1 = \frac{\varphi_g P_{00}}{A_{00} - \varphi_g P_{00}} \cdot \frac{\gamma'}{1-\gamma'} \\ \gamma' = \frac{\gamma A_{00}}{A_{00}/P_{00} - \varphi_g} \end{array} \right. \quad (14)$$

The quantities A_{00} and φ_g occur in the constants a_1 , b_1 and γ' in such a way that they (by extension of the fractions with a = the water content of the solution in grams) can be replaced by the absolute quantities n_t and Φ_g . The physical significance of γ' can clearly be seen from the expression $\alpha_A = \alpha_A^0(1-\gamma'Y)$ which shows how the absorption coefficient of acetylene changes with the conversion degree Y . The last formula in (14) has the same meaning but shows how γ' is computed from the known γ -value 0.0759 atm^{-1} and the data valid for the individual experiment: A_{00} (or n_t), P_{00} and φ_g (or Φ_g).

The first term — the main term — here has a coefficient a_1 whose closest physical meaning is the partition quotient (gas + liquid)/liquid of acetylene at the end of the experiment, when $HCl_t = HCl_t^0 - A_{00}$. It is for several reasons suitable to split the first term to get a main term with a coefficient stating the partition quotient at the start of the experiment.

The relation will then have the following form:

$$\left\{ \begin{array}{l} \frac{A_{00}}{A_d} = a_2(1-Y)^{-1} + b_2\gamma'[(1-Y)^{-1} - (1-\gamma'Y)^{-1}] \\ \text{where } a_2 = A_{00}/(A_{00} - \varphi_g P_{00}) \\ b_2 = \frac{\varphi_g P_{00}}{A_{00} - \varphi_g P_{00}} \cdot \frac{1}{1-\gamma'} \end{array} \right. \quad (15)$$

where γ' has the same meaning as in (14). Also in a_2 and b_2 the quantities A_{00} and φ_g can be simultaneously replaced by n_t and Φ_g .

The quantity

$$I_c \equiv \int_0^Y \frac{A_{00} \cdot dY}{A_d} \quad (16)$$

can easily be computed by integration of (15) with the result

$$\begin{cases} I_c = -a_2 \ln(1-Y) + b_2 R(\gamma', Y) \\ \text{containing the "correction function"} \\ R(\gamma', Y) \equiv \ln(1-\gamma'Y) - \gamma' \ln(1-Y) \end{cases} \quad (17)$$

The constants a_2 , b_2 and γ' have the same meaning as above.

The pseudo first order "constant" κ_c finally is obtained from

$$\kappa_c = \frac{I_c - I_c^0}{t} \quad (18)$$

The introduction of the $R(\gamma', Y)$ -function which has been prepared by the term "splitting" in (15) gives the advantage that the main term becomes independent of the γ' -correction. The quotient R/t vanishes when t approaches zero. At decreasing conversion degree the correction thus becomes negligible, a fact that cannot be seen numerically if an I_c -function is used, obtained by integration of the not "split" formula (14).

The result of such a calculation appears from Table 2 and Fig. 2 with data from experiments 11 and 14.

Table 2. Computation of conversion degree Y etc., the integral I_c and the quantity κ_c . Experiment 11.

Time h	Y_p %	Y %	Z %	$-a_2 \times$ $\ln(1-Y)$	I_c	$10^3 \times \kappa_c$ h^{-1}
0	0.23	0.23	0	0.0028	0.0028	—
1.600	5.90	5.85	3	729	729	4.38 ± 0.04
2.429	8.70	8.64	4	1093	1093	4.38 ± 3
4.886	16.27	16.16	8	2133	2134	4.310 ± 15
5.276	17.55	17.43	9	2317	2318	4.340 ± 14
5.724	18.82	18.69	10	2504	2505	4.328 ± 13
6.200	20.21	20.08	11	2712	2713	4.331 ± 13
9.372	28.72	28.55	15	4068	4071	4.314 ± 9
10.058	30.46	30.29	16	4366	4370	4.317 ± 9
18.92	49.08	48.87	27	8116	8128	4.280 ± 9
20.47	51.82	51.61	29	8783	8796	4.284 ± 6
21.63	53.74	53.54	30	9275	9290	4.282 ± 6
22.85	55.67	55.47	31	0.9789	9805	4.279 ± 6
24.13	57.58	57.38	33	1.0319	1.0337	4.273 ± 6
25.36	59.37	59.17	34	1.0838	1.0858	4.270 ± 6
26.88	61.46	61.26	35	1.1474	1.1496	4.266 ± 6
31.89	67.51	67.33	40	1.3536	1.3565	4.245 ± 6
42.97	77.71	77.57	48	1.8087	1.8134	4.214 ± 7
45.10	79.33	79.20	50	1.9000	1.9051	4.218 ± 7
47.54	80.94	80.81	51	1.9974	2.0029	4.207 ± 7
49.26	82.02	81.90	52	2.0682	2.0740	4.204 ± 7
50.64	82.85	82.73	53	2.1250	2.1311	4.203 ± 7
68.48	90.57	90.50	62	2.8482	2.8577	4.169 ± 10
72.03	91.65	91.59	63	2.9956	3.0058	4.169 ± 10
95.49	96.17	96.14	70	3.9379	3.9530	4.137 ± 17
95.97	96.22	96.19	71	3.9537	3.9689	4.133 ± 17

The change of κ_c during an individual experiment is evidently significant — as can be seen from Table 2. The values show a decreasing trend approaching 4 or 5 %. According to the relation

$$\kappa_c = \frac{1}{t} \int_0^t f_c dt \quad (19)$$

f_c decreases too and the change is greater than in κ_c . In spite of that there is no need to assume that f_c depends upon A_d — this would mean that the main hypothesis was given up. There is a co-variation of HCl_t due to the HCl consumption during the reaction amounting to 3.4 % in experiment 11 (the basis of Table 2) and a comparison between different experiments immediately indicates that κ_c and f_c have a marked HCl_t -dependence.

An approximate relation between f_c and HCl_t is required to render the effect at the kinetic calculation. It appears clearly from the tentative experiments in Part II that the strong HCl_t -dependence of the reaction velocity follows a peculiar functional relation. There is no use testing any conventional assumption of a first or second order dependence on HCl_t .

But the initial value of the κ_c — determined by a graphical method described in the next chapter — gives a good approximation of the f_c -value, valid at the start of the experiment where $HCl_t = HCl_t^0$.

DETERMINATION OF THE INITIAL VALUE κ_c^0

The quantity κ_c^0 , defined by:

$$\kappa_c^0 \equiv \lim_{Y \rightarrow 0} \kappa_c \quad (20)$$

can be determined by graphic extrapolation in a diagram where the κ_c -values of the experiment are plotted against the conversion degree Y . The relation is tolerably linear at low conversion degree. The pseudo first order constants

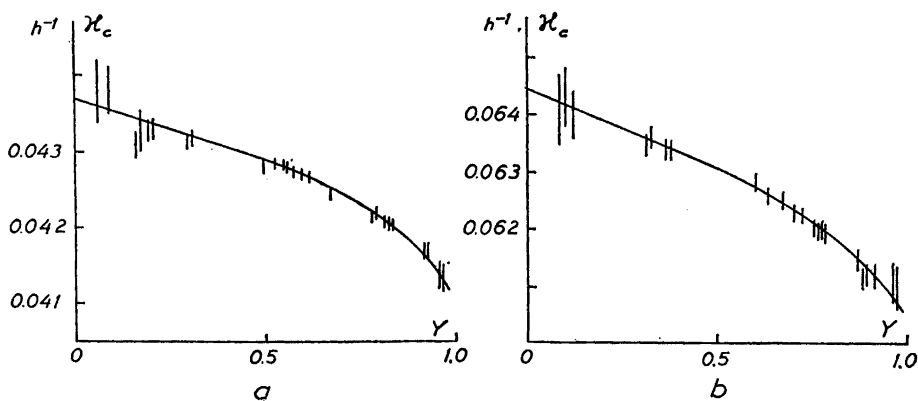


Fig. 3. The pseudo first order "constant" κ_c as a function of the conversion degree Y . a: Experiment 11; 7.25 m HCl; CuCl(s). b: Experiment 14; 9.10 m HCl; CuCl(s).

κ_c are presented in Fig. 3 as functions of the conversion degree Y — data from the experiments 11 and 14.

A better result is obtained by plotting κ_c against the conversion parameter Z , defined by

$$Z \equiv 1 + \frac{Y}{\ln(1-Y)} \quad (21)$$

The method has been used for a similar purpose in Part II as well (p. 1240) and starts from the assumption that the f_c -changes during the experiment can be satisfactorily rendered by a correction of the linear form $f_c = f_c^0 (1 - \rho B)$ where ρ is a constant. It is then easy to prove that the κ_c value changes during the course of the experiment according to

$$\kappa_c = \kappa_c^0 - \frac{1}{t} \int Y dt \quad (22)$$

When computing the Y value that enters into the correction term it is justified to use an approximate first order formula $\ln(1-Y) = -kt$. Without further approximations we then get:

$$\kappa_c = \kappa_c^0 = \rho Z \quad (23)$$

In Fig. 4 the quantity κ_c is given as a function of the Z -parameter for the experiments 11 and 14. In the entire diagram the relation can be considered linear — within the observation errors.

When fitting the extrapolation line we have to consider — *cf.* Fig. 4 — that both the error (derived from P) that varies from point to point and the constant one (from P_0) are larger in the beginning of the experiment, *i.e.* at low Z -values. To facilitate the judgement the points of the diagram have been marked with vertical lines showing the dispersion ($\pm \sigma$) which can be calculated *a priori* from $\sigma(P)$.

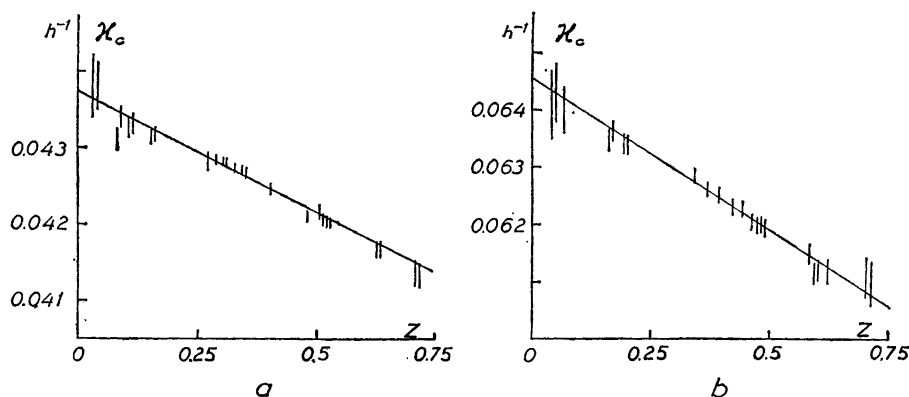


Fig. 4. The quantity κ_c as a function of the conversion parameter Z . Graphic determination of κ_c^0 . a: Experiment 11; 7.25 m HCl; CuCl(s). Extrapolation gives $\kappa_c^0 = 0.0437 \text{ h}^{-1}$. b: Experiment 14; 9.10 m HCl; CuCl(s). Extrapolation gives $\kappa_c^0 = 0.0645 \text{ h}^{-1}$.

As can be seen the points adhere well to the drawn straight line, nearly all of them lying at a distance less than σ .

Table 3 shows that as many as 24 of the 25 κ_c -values in experiment 11 fall within $\pm \sigma$ from the extrapolation line and the remaining one within

Table 3. The deviations of the κ_c -values from the extrapolation line. Accepted κ_c^0 -values. Their independence of P_0 and A_d^0 .

HCl_t m	Note	Expt. No.	κ_c^0 h^{-1}	Number of measurements		
				Totally	Within $\pm \sigma$	Within $\pm 2\sigma$
5.53	—	9	0.0262	24	17	24
6.50	—	10	0.0361	18	14	18
7.25	—	11	0.0437	25	24	24
7.94	—	7	0.0514	16	12	16
8.57	—	12	0.0583	32	25	29
9.05	P_0 170 mm	5	0.0638	20	20	20
9.06	P_0 305 mm	6	0.0637	13	11	13
9.05	P_0 461 mm	13	0.0636	14	11	14
9.10	—	14	0.0645	23	22	23
10.05	—	15	0.0756	23	20	23

$\pm 2\sigma$. The table includes corresponding data from all other experiments even those which are presented in the next paper in this series. The extrapolation line can in all cases be drawn very close to the observed points and the deviations are mostly as small as in experiment 11. (Perhaps the *a priori* uncertainty $\sigma(P)$ has been somewhat overestimated.)

Also in other kinetic investigations on nearly first order reactions we have found it advantageous to use the Z -function. At treatment of reactions of the type $dY/dt = k(1-Y)(1-\Delta Y)^p$, where p is a positive or negative integer and $\Delta < 1$, the Z -function could be used in a similar way for a simultaneous determination of k and Δ .

The normally used method of estimating the initial velocity — or the initial value of the kinetic “constant” — of a nearly first order reaction is to determine graphically the concentration time derivative at the start. Even in our case the quantity κ_c^0 can be calculated from a graphically determined initial velocity $(dP/dt)_0$ but the accuracy is unsatisfactory. Better results will be obtained if we use a diagram where $\ln(P_\infty - P)$ is plotted against t . But the recommended extrapolation method using the Z -function as described above gives κ_c^0 -values of considerably higher accuracy. The difference is of special importance in this work because of the high accuracy of the primary data and also because of the risk of systematic errors in the very early readings.

By examining whether the slope of the straight line coincides with the one that can be predicted from an obtained κ_c^0 - HCl_t^0 -relation we can test the hypothesis that the HCl consumption is the only cause of the κ_c -changes in the individual experiment. Such a procedure is used in Part II. But here we are content with the use of the Z -function for the described extrapolation.

But it is of interest to emphasize some cases with identical HCl_t^0 but different A_d^0 . If the main hypothesis is valid, the quantity κ_c^0 — that may be regarded as an approximate f_c -value — should be independent or at least almost independent on A_d^0 . This is verified by a comparison — see Table 3 — between experiments 5, 6, and 13 with identical HCl_t^0 but with different A_t^0 -values (approximately proportional to P_0).

EXPERIMENTS

Apparatus and experimental techniques are fully described in Part I where also details can be found on the preparation of the catalyst solution from cuprous chloride of high purity, the elimination of air oxidation, and the calibration with vinyl chloride. Described are also the computation of the theoretical end pressure, the determination of the start pressure P_0 by linear or "logarithmic" extrapolation, the calculation of the equilibrium pressure P_{∞} , and finally the estimation of the $\sigma(P)$ of the individual series.

Experiment 5: CuCl(s); 9.05 m HCl; $P_0 = 169.5$; 25.0°C

Procedure and experimental data in Part II.

The pressure fall due to the vinyl chloride loss during the end period approaches the constant velocity $0.010 \text{ mm}\cdot\text{h}^{-1}$ (at 530 mm). This gives the correction factor $\xi = 2.74 \times 10^{-5} \text{ h}^{-1}$. The corrections computed according to (8) are + 0.1 mm for pressure values read after 30 and 31 h, + 0.2 mm at 36 and 38 h and + 0.3 mm between 47 and 53 h. The corrected values $t(\text{h})-P(\text{mm Hg uncorr.})$ of the end period are: 95.0–531.3; 100.0–532.1; 103.0–532.4; 122.0–534.6; 143.0–535.3; 146.0–535.9; 147.0–535.7; 151.0–535.5; 170.0–536.2; 175.0–536.3; 220.5–536.3; 263.5–535.5.

Computed values. Gas phase capacity $\Phi_g = (5.666 \pm 0.005) \times 10^{-6} \text{ mole}\cdot\text{mm}^{-1}$. The corrected time pressure curve ends at $P_{\infty} = 536.0 \pm 0.3$ which is used in the calculation. (Further data in Part II.) Constants for (10) and (15): $\psi = 0.0075$; $\gamma' = 0.0223$; $a_2 \cdot \ln 10 = 3.0901$; $b_2 \cdot \ln 10 = 0.806$.

Experiment 6: CuCl(s); 9.06 m HCl; $P_0 = 305.0$; 25.0°C

Procedure and experimental data in Part II.

The pressure fall during the end period approaches the constant velocity $0.034 \text{ mm}\cdot\text{h}^{-1}$ which gives the correction factor $\xi = 5.22 \times 10^{-5} \text{ h}^{-1}$. Corrections computed according to (8) are + 0.1 mm for the six last pressure values of the main period. The corrected values $t-P$ of the end period are: 95.5–951.7; 98.0–952.5; 99.0–952.5; 103.0–954.5; 119.5–958.8; 127.0–958.9; 143.5–960.0; 147.5–960.1; 151.5–959.9; 169.0–960.0; 175.5–960.5; 193.5–960.2; 197.0–960.5; 263.5–960.4.

Computed values. Gas phase capacity $\Phi_g = (5.683 \pm 0.005) \times 10^{-6} \text{ mole}\cdot\text{mm}^{-1}$. The corrected time pressure curve ends at $P_{\infty} = 960.4$ that is used in the calculation. (Further data in Part II.) Constants for (10) and (15): $\psi = 0.0137$; $\gamma' = 0.0404$; $a_2 \times \ln 10 = 3.0970$; $b_2 \cdot \ln 10 = 0.828$.

Experiment 7: CuCl(s); 7.94 m HCl; $P_0 = 261.0$; 25.0°C

Data in Part IV.

Experiment 9: CuCl(s); 5.53 m HCl; $P_0 = 168.3$; 25.0°C

Data in Part IV.

Experiment 10: CuCl(s); 6.50 m HCl; $P_0 = 249.9$; 25.0°C

Data in Part IV.

Experiment 11: CuCl(s); 7.25 m HCl; $P_0 = 254.7$; 25.0°C

Procedure: 14.0 g CuCl and 2.0 g Cu are mixed with hydrochloric acid whose water content at the acetylene addition is calculated as 26.03 g. Vapour pressure 14.5 mm, reading after 18 h for tightness check gives 14.5 mm. After calibration with nitrogen and calibration and tightness check (1015.0 → 1014.3 mm during 17 h) with vinyl chloride, acetylene is added in two portions with a time difference of 0.0370 h. The first portion contains 3.7 millimoles; totally 6.438 ± 0.008 millimoles are added. Timing is started at the last addition. Readings $t-P$ during the start period: 0.1528–260.1; 0.2306–261.6; 0.3111–264.0; 0.4000–266.1; 0.4917–269.0; 0.6778–273.9; 0.8472–278.5; 1.0389–283.9; 1.3417–292.0. Main period: 1.600–298.9; 2.429–320.7; 4.886–379.7; 5.276–389.7; 5.724–399.6; 6.200–410.3(410.4); 9.372–476.7(476.8); 10.058–

490.2(490.3); 18.924—635.3(635.5); 20.467—656.6(656.8); 21.631—671.5(671.8); 22.850—686.5(686.8); 24.126—701.4(701.7); 25.363—715.4(715.7); 26.881—731.6(732.0); 31.886—778.6(779.1); 42.965—857.8(858.6); 45.099—870.3(871.3); 47.539—882.8(883.8); 49.264—891.1(892.2); 50.639—897.6(898.7); 68.481—957.1(958.9); 72.033—965.4(967.3); 95.494—999.6(1002.5); 95.969—1000.0(1002.9). End period: 115.0—1013.3(1016.9); 119.0—1015.1(1018.0); 122.5—1016.9(1020.8); 139.0—1020.7(1025.3); 143.0—1022.0(1026.7); 147.0—1022.0(1026.9); 163.0—1023.9(1029.4); 168.0—1024.3(1030.0); 170.5—1024.3(1030.1); 188.0—1025.4(1032.0); 212.0—1025.0(1032.5); 215.0—1025.0(1032.6); 242.0—1023.3(1032.0); 274.0—1022.0(1032.1); 284.0—1021.5(1032.0); 290.5—1021.4(1032.1); 314.0—1020.9(1032.6).

The vinyl chloride loss during the end period gives a pressure fall that approaches the constant velocity 0.041 mm/h at 1025 mm giving the correction factor $\xi = 5.29 \times 10^{-4} \text{h}^{-1}$. Pressure values corrected according to (8) are given within parentheses in the table above.

Computed values. Undissolved amount of CuCl ca. 8.5 g; gas phase capacity $\Phi_g = (4.415 \pm 0.006) \times 10^{-6}$ mole.mm⁻¹. Theoretical end pressure according to the vinyl chloride calibration 1035.1 ± 1.8 , highest pressure measured in the acetylene experiment 1025.4; corrected values at $t > 200$ h are constant within $P_{\infty m} = 1032.4 \pm 0.4$. The last value is used at the calculations. The start pressure $P_0 = 254.7$ and the equilibrium pressure $P_{00} = 252.9$; $\sigma(P) = \pm 0.4$ mm. Constants for (10) and (15): $\psi = 0.0082$; $\gamma' = 0.0305$; $a_2 \cdot \ln 10 = 2.7861$; $b_2 \cdot \ln 10 = 0.499$.

Experiment 12: CuCl(s); 8.57 m HCl; $P_0 = 244.5$; 25.0°C

Data in Part IV.

Experiment 13: CuCl(s); 9.05 m HCl; $P_0 = 461.0$; 25.0°C

Procedure: 16.0 g CuCl and 2.0 g Cu are mixed with hydrochloric acid, whose water content at the acetylene addition is calculated as 16.89 g. Vapour pressure 12.8 mm, reading after 23 h 13.3 mm. After calibration with nitrogen and calibration and check of tightness (983.4 → 982.1 during 19 h) with vinyl chloride, acetylene is added in five portions: 3.74 millimoles at $t = -0.3986$ h; 2.21 at -0.2528 ; 1.36 at -0.1958 ; 1.53 at -0.0764 and 1.13 at $t = 0.0000$ h. Totally 10.027 ± 0.010 millimoles are added. Readings $t-P$ during the start period: 0.1375—468.5; 0.2250—471.9; 0.3208—475.9; 0.4069—480.1; 0.5000—484.5; 0.5931—488.5; 0.6778—492.2. Main period: 0.8500—499.9; 1.0194—507.3; 1.6125—532.0; 2.306—561.5; 2.839—582.4; 3.363—602.3; 3.831—620.5; 4.390—641.0; 4.915—659.7; 5.444—678.4; 6.219—704.9; 22.579—1075.5; 23.086—1083.1; 23.653—1091.3.

Correction for vinyl chloride loss is — due to the short experiment time — not necessary.

Computed values. Undissolved amount of CuCl ca. 11.0 g. Gas phase capacity $\Phi_g = (5.707 \pm 0.007) \times 10^{-6}$ mole.mm⁻¹. Theoretical end pressure according to the vinyl chloride calibration $P_{\infty m} = 1416.2 \pm 2.5$, that is accepted for the kinetic calculation. The start pressure, determined by linear extrapolation is $P_0 = 461.0$ and the equilibrium pressure $P_{00} = 450.7$. The dispersion $\sigma(P) = \pm 0.3$ mm. Constants for (10) and (15): $\psi = 0.0210$; $\gamma' = 0.0605$; $a_2 \cdot \ln 10 = 3.0970$; $b_2 \cdot \ln 10 = 0.846$.

Experiment 14: CuCl(s); 9.10 m HCl; $P_0 = 299.6$; 25.0°C

Procedure: 16.0 g CuCl and 2.0 g Cu are mixed with hydrochloric acid whose water content at the acetylene addition is 16.82 g. Vapour pressure 12.7 mm, after 4 h unchanged value. After calibration with nitrogen and calibration and check of tightness (1152.0 → 1150.8 during 17 h) with vinyl chloride, acetylene is added in two portions with a time difference of 0.1095 h. The first addition contains 3.82 millimoles; totally 6.350 ± 0.008 millimoles are added. Timing is started at the last addition. Readings $t-P$ during the start period: 0.1445—310.9; 0.2167—311.2; 0.3025—313.5; 0.3833—315.6; 0.4625—318.2; 0.5444—320.9; 0.7111—325.6; 0.8833—331.2; 1.0681—337.0; 1.2833—344.1. Main period: 1.5639—353.1; 2.047—368.9; 2.628—387.0; 7.529—520.5; 7.928—530.4; 8.514—543.4; 8.983—554.0; 9.533—566.2; 18.753—725.5(725.7); 20.786—751.1(751.3); 22.896—775.9(776.2); 25.182—799.6(799.9); 26.635—813.5(813.9); 29.235—835.7(836.2); 30.350—844.5(845.0); 31.457—853.1(853.6); 31.964—856.7(857.2); 43.636—920.9(921.7); 45.376—928.3(929.2); 47.931—936.5(937.5); 50.457—944.6(945.7); 68.432—981.6(983.3); 70.633—984.3(986.0). End period: 114.7—1006.0(1009.2); 118.7—1005.9(1009.3); 170.4—1006.1(1011.3); 188.0—1006.1(1011.9); 191.0—1005.8(1011.7); 212.0—1005.5(1012.2); 218.5—1005.4(1012.2); 238.2—1004.6(1012.1); 239.9—1003.9(1011.5).

The pressure fall during the end period approaches the constant velocity $0.035 \text{ mm}\cdot\text{h}^{-1}$ (at 1000 mm), corresponding to the correction factor $\xi = 4.91 \times 10^{-6} \text{ h}^{-1}$. Pressure values corrected according to (8) are given within parentheses in the table above.

Computed values. Undissolved amount of CuCl ca. 11.0 g. Gas phase capacity $\Phi_g = (4.931 \pm 0.007) \times 10^{-8} \text{ mole}\cdot\text{mm}^{-1}$. Theoretical end pressure according to the vinyl chloride calibration 1014.5 ± 2.8 , highest pressure measured in the acetylene experiment 1006.1. The corrected time pressure curve ends at 1012.2, a value that is accepted as P_{com} in the calculation. The start pressure is determined by logarithmic extrapolation also using the three first points of the main period with the result $P_0 = 299.6$. The equilibrium pressure $P_{00} = 297.3$. The dispersion $\sigma(P) = \pm 0.4 \text{ mm}$. Constants for (10) and (15): $\psi = 0.0123$; $\gamma' = 0.0386$; $a_2 \cdot \ln 10 = 2.9934$; $b_2 \cdot \ln 10 = 0.719$.
Experiment 15: CuCl(s); 10.05 m HCl; $P_0 = 309.4$; 25.0°C

Data in Part IV.

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