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RATES OF HYDROLYSIS OF ETHYLENE DIBROMIDE (EDB)

Final Report

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RATES OF HYDROLYSIS OF
ETHYLENE DIBROMIDE (EDB)

Prepared for

INDUSTRIAL COMMITTEE OF THE

ETHYLENE DIBROMIDE RESEARCH

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INTRODUCTION

This study was designed to determine hydrolysis rates of ethylene dibromide (EDB) at two temperatures, each with three pH regiments. These six test regimes, all conducted in darkness, were expected to provide estimates of EDB half-life and the applicable rate law. Product degradates were to be identified by gas chromatographic/mass spectrometric techniques and/or ion chromatography.

Consider a simple case in which the aqueous hydrolysis of an alkyl bromide, R-Br, is found to follow the kinetics

$$\text{Rate} \propto [\text{R-Br}].$$

Although $[H_2O]$ does not figure in the rate equation, one cannot conclude that the rate-determining step does not involve the participation of water. If water is being used as the solvent (as is the case in this study), its concentration would remain virtually unchanged whether or not it actually participated in the reaction.

The participation of water might be revealed by carrying out the hydrolysis in another solvent with only a small concentration of water; then the hydrolysis may be found to follow the kinetics

$$\text{Rate} \propto [\text{R-Br}][H_2O].$$

However, if this alteration of the environment changes the actual mechanism by which the reaction proceeds, then no information is gained concerning the reactions taking place in the initial aqueous solution.

A brief discussion of the theory of chemical kinetics follows, along with a presentation of the techniques employed to establish rates and calculate half-lives.

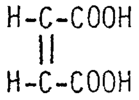
CHEMICAL KINETICS

Chemical kinetics is concerned with the velocity of reactions and with the intermediate steps by which reactants are ultimately converted into products.

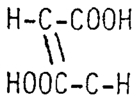
Molecularity of Reactions

A unimolecular reaction is one in which only one molecule reacts at a time. Examples are:

$$Br_2 \longrightarrow Br^{\bullet} + Br^{\bullet}$$



$$\begin{array}{c}\text{H-C-COOH}\\ \| \\ \text{H-C-COOH}\end{array}$$



$$\begin{array}{c}\text{H-C-COOH}\\ \backslash\backslash \\ \text{HOOC-C-H}\end{array}$$

A bimolecular reaction is one in which two molecules (either of the same or different kinds) react. Examples are:

$$H_2 + Br_2 \longrightarrow 2\ HBr$$

$$2\ HI \longrightarrow H_2 + I_2$$

A termolecular reaction takes place as a result of the simultaneous collision of three molecules. An example is:

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

First Order Reactions

A first order reaction is one in which the rate of the reaction is found by experiment to be directly proportional to the concentration of the reacting substance. It follows from the law of mass action that at constant volume:

$$-\frac{dc}{dt} = kC,$$

in which:

c = Concentration of reactant

t = Time

k = Constant (called the rate constant)

1. $-\frac{dc}{dt}$ = rate of decrease in concentration with time.

Rearranging and integrating:

2. $-\frac{dc}{c} = k\ dt$

$$-\ln c = kt + \text{constant}$$

3. $$\log C = \frac{-k}{2.303}t - \frac{\text{constant}}{2.303}$$

Thus, if logC is plotted versus t, a straight line is obtained whose slope is -k/2.303. However, if equation 2. is integrated between the limits, c_1 at t_1 and C_2 at t_2:

4. $$-\int_{c_1}^{c_2} \frac{dc}{c} = k\int_{t_1}^{t_2} dt$$

5. $$-\ln \frac{C_2}{C_1} = k(t_2-t_1)$$

6. $$\ln \frac{C_1}{C_2} = k(t_2-t_1)$$

7. $$k = \frac{2.303}{t_2-t_1} \log \frac{C_1}{C_2}$$

in which: C_1 = Concentration of reactant at time t_1

C_2 = Concentration of reactant at time t_2

Equation 7 can be modified as follows:

8. $$k = \frac{2.303}{t} \log \frac{C_o}{c}$$

in which: Co = Concentration at the beginning of reaction (i.e., t=o)
C = Concentration left at time t.

If the initial concentration of reactant is represented by a and the amount reacted in time t is represented by x, then a-x is the concentration remaining after time t, and:

9. $$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

It is evident from equations 8. and 9. that k has the units of time $^{-1}$. The "half-life)", $t_{1/2}$ is the time necessary for half of a given quantity of material to react. Then:

10. $k = \frac{2.303}{t_{1/2}} \log \frac{1}{1/2}$

11. or $t_{1/2} = \frac{0.693}{k}$

In general, if a reaction has been shown to be of first order it can be assumed to be unimolecular. A reaction is of first order if:

1. Reasonably constant values for k are obtained when the experimental data are substituted into equations 7., 8., or 9., or

2. A straight line is obtained when logC is plotted versus t (equation 3.).

Example. For the reaction

$$A \longrightarrow B + C$$

the following data were obtained

t in sec	0	900	1800
Conc. of A	50.8	19.7	7.62

Prove that the reaction is of first order

$$k = \frac{2.30}{t} \log \frac{Co}{C}$$

$$k = \frac{2.30}{900} \log \frac{50.8}{19.7} = 0.00105 \text{ sec}^{-1}$$

$$k = \frac{2.30}{1800} \log \frac{50.8}{7.62} = 0.00105 \text{ sec}^{-1}$$

Since the two values of k agree, the reaction is of the first order.

Example. In the example above, calculate how long it would take for half of the original material to decompose.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.00105} = 660 \text{ sec}$$

Second Order Reactions

If the rate of a reaction depends on the concentration of two substances, the reaction is of second order. If:

$$A + B \qquad AB$$

12. Then $-\frac{dcA}{dt} = -\frac{dCB}{dt} = K.C_A.C_B$

$-\frac{dC_a}{dt}$ = rate at which the concentration of A decreases,

$-\frac{dC_B}{dt}$ = rate at which the concentration of B decreases

k = rate constant

C_A = Concentration of A,

C_B = Concentration of B.

If the initial molar concentrations of A and B are represented by a and b, respectively, and if x denotes the amount of A and B reacting in time t, then:

13. $$\frac{dx}{dt} = k\ (a-x)(b-x)$$

However, if a=b, then

14. $$\frac{dx}{dt} = k\ (a-x)^2$$

Integrating:

$$\frac{dx}{(a-x)^2} = k \bullet dt$$

15. $$\frac{1}{a-x} = kt + C$$

in which C = constant of integration. The constant C may be evaluated by setting x=o when t=o. Then:

$$\frac{1}{a-o} = k\ (o) + C$$

16. or $C = \frac{1}{a}$

Substituting into equation 15:

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\frac{1}{a-x} - \frac{1}{a} = kt$$

17. $$\frac{a}{a(a-x)} - \frac{a-x}{a(a-x)} = kt$$

18. $$k = \frac{1}{t} \bullet \frac{x}{a\,(a-x)}$$

If the concentrations are expressed in moles/liter and time is expressed in seconds, then k has the units of liters/mole-seconds.

When half of the original material has reacted, x=a/2 and:

$$k = \frac{1}{t_{1/2}} \bullet \frac{a/2}{a\left(a-\frac{a}{2}\right)} = \frac{1}{t_{1/2}} \bullet \frac{1}{a}$$

19. or $$t_{1/2} = \frac{1}{k.a}$$

It must be remembered that equations 18. and 19. apply only when a=b.

If a=b then equation 13. must be integrated. This integration gives the following:

20. $$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

In general, a reaction may be assumed to be bimolecular if it is of second order. A reaction is of second order if:

1. Reasonably constant values of k are obtained when experimental data are substituted into equations 18. (if a=b) or 20. (if a=b) or

2. A straight line is obtained when 1/a-x is plotted versus time (true only if a=b)

An example of a second order reaction is the saponification of ethyl acetate by sodium hydroxide.

$$CH_3COOC_2H_5 + OH^- = CH_3COO^- + C_2H_5OH$$

Example. A certain bimolecular reaction in which a=b=1 mole/liter is 10% complete in 10 minutes. How long does it take the reaction to be 50% complete?

$$k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

$$k = \frac{1}{10}\,\frac{0.1}{(1)(1-0.1)}$$

$$k = \frac{0.1}{9} = 0.011 \text{ liter/mole-minute}$$

$$\text{and } t_{1/2} = \frac{1}{k.a} \qquad \frac{1}{(0.0111)(1)} = 90 \text{ minutes}$$

<u>Third Order Reactions</u> exist, but are rare.

<u>Zero Order Reactions</u>

A reaction is of zero order if the reaction rate is unaffected by concentrations. This is possible if the rate is determined by some other limiting factor, as absorption of light, or if the concentration is kept constant (as in a saturated solution).

For such a reaction:

$$-\frac{dC_a}{dt} = k$$

and $C_A = -kt + \text{a constant}$

A plot of concentration versus time yields a straight line. This criterion can be used to prove that a reaction is of zero order.

<u>Complex Reactions</u>

Only a few reactions are straightforward first-, second-, or third order reactions. Instead, several reactions are usually taking place at one time. There are three important types of complications.

<u>Consecutive Reactions</u>. A consecutive reaction may be represented as:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C,$$

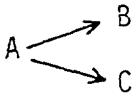
in which k_1 is the rate constant for the first step and k_2 is the rate constant for the second step. Consecutive reactions are very common. For example, the oxidation of ethane to CO_2 and H_2O really passes through a series of intermediate steps in which alcohols, ketones, acids, etc., are formed.

Reverse Reactions. A reverse reaction may be represented as:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

in which k_1 is the rate constant for the forward reaction and k_2 is the rate constant for the reverse reaction. If the rate of the reverse reaction is appreciable, it must be taken into account in the evaluation of k_1 if a correct value is to be obtained.

Side Reactions. A side reaction may be represented as:



These are especially common in organic chemistry. For example, the nitration of phenol gives both o-nitrophenol and p-nitrophenol. The amount of each isomer obtained depends on k_1 and k_2. The organic chemist tries to suppress undesirable side reactions by appropriate control of temperature, pressure, catalyst, and other factors.

EXPERIMENTAL

Solutions of EDB in aqueous buffers were prepared as follows. The EDB was weighed in a small glass thimble and was dropped in a 1-liter volumetric flask filled to the mark with the corresponding buffer. A magnetic stirrer bar was added; the flask was then stoppered and agitated overnight or until the glass thimble was broken into small pieces and the EDB completely dissolved. The water and the glassware were sterilized in an autoclave.

Three solutions were prepared: one in the buffer of pH5, 95.6 ppm; the second in the buffer of pH7, 88.8 ppm; and the third in the buffer of pH9, 85.1 ppm.

At the same time, a standard solution was prepared in distilled water, 96 ppm. Several glass ampules were filled with each of the EDB solutions and sealed with a propane-oxygen torch. Each ampule had approximately 1 cm^3 headspace.

A number of ampules of each buffer solution were placed in an incubator maintained at 25±1°C and in another maintained at 45±1°C. A number of ampules were also filled with the standard EDB solution, sealed and kept in the refrigerator at 4°C.

One ampule for each pH and temperature (total of six) was withdrawn from the incubators and analyzed for EDB concentration on days 0, 30, 60, 95 and 140. Each ampule was broken and 0.4μl samples were withdrawn with a microsyringe for chromatographic analysis. Six replicate analyses were performed from each ampule, the ampule being capped between samplings. The mean of the six analyses was calculated and used as the concentration at that day.

Detection response was standardized for each analysis run using 0.4μl reference solution of 96 ppm EDB. A new ampule of the standard EDB solution was withdrawn from the refrigerator on each analysis day. The EDB concentration in the buffer solutions was calculated by comparing the area of the sample peak to the area of the reference standard of known concentration.

Temperatures and pH regiments were as follows:

Incubation temperature in °C	pH
25.0	5.0
45.0	5.0
25.0	7.0
45.0	7.0
25.0	9.0
45.0	9.0

The ampules were discarded after analysis.

Calculations

$$C_{sample} = \frac{C_{standard} \times A_{sample} \times V_{standard}}{A_{standard} \times V_{sample}}$$

where C = Concentration

V = Volume (0.4µl)

A = Area given in units generated by the GC integrator.

Product Half-Life Calculation

The half-life for the decomposition of EDB was calculated assuming first that the reaction follows zero order kinetics and second that the reaction follows first order kinetics. Since all the experimental results point towards a zero or first order rate, the half-life was not calculated for a higher order.

Zero Order: A plot of concentration vs. time was made. The plot was treated as a straight line. A straight line was drawn from the point of half-concentration on the x-axis and parallel to the y-axis (the time axis). From the point of intersection of that line and the concentration-time plot curve, a perpendicular to the y-axis was drawn. The intersection point on the y-axis gives the half-life $t_{1/2}$. Table IX shows the half-life of the hydrolysis of EDB for the six sets of concentrations assuming that the order of hydrolysis was zero.

First Order: Making the assumption that the hydrolysis of EDB follows first order reaction, the half-life was calculated from the formula

$$t_{1/2} = \frac{0.693}{K}$$

Tables III through VIII list the half-lives of EDB hydrolysis for the six combinations of pH and temperature.

DISCUSSION

In this study we have attempted to determine the hydrolysis rate of ethylene dibromide, to identify the order of the reaction, and to calculate the half-life under each set of experimental conditions.

Ethylene dibromide, however, is a bifunctional molecule capable of undergoing a number of different reactions either concurrently or sequentially; thus the hydrolysis rate should not be expected to comply with any simple rate law.

For example, either or both bromine atoms could be substituted by a hydroxyl group via a unimolecular reaction of the SN-1 type or by a bimolecular SN-2 type reaction.

$$Br-CH_2-CH_2-Br \xrightarrow[\text{or SN2}]{\text{SN1}} Br-CH_2CH_2-OH \xrightarrow[\text{Sn-2}]{\text{Sn-1}}$$

ethylene dibromide bromohydrin

$$HO-CH_2-CH_2-OH$$

glycol

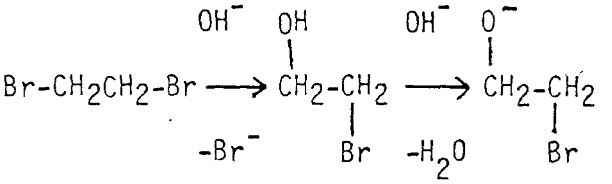
to yield the Bromohydrin and then the ethylene glycol.

Although the high polarity of the solvent will favor the unimolecular mechanism SN-1, the structure of a primary alkyl bromide will favor a bimolecular type mechanism such as SN-2.

The overall conditions therefore are not optimum for either SN-1 or Sn-2 type displacement, and although they both may be operating, their contribution to the hydrolysis rate would be expected to be small.

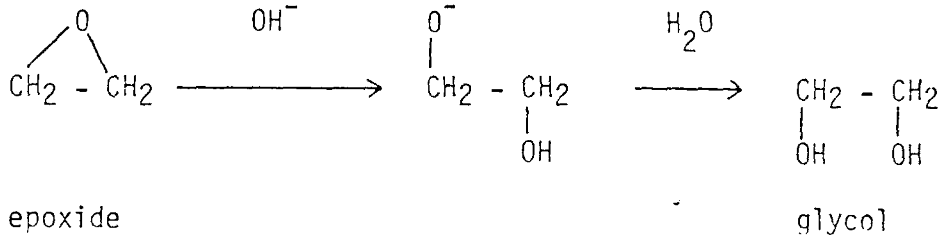
Another mechanism expected to be very important in the hydrolysis of ethylene dibromide is "neighboring group participations."

One bromine atom is replaced by a hydroxyl group via SN-1 or SN-2 type of displacement reaction. The newly introduced hydroxyl group is further converted into an alcoxide by the base; the alcoxide in turn displaces internally the second bromine atom of the ethylene dibromide, yielding an epoxide. The epoxide is then converted to the ethylene glycol by the base.



$$Br-CH_2CH_2-Br \xrightarrow[-Br^-]{OH^-} \overset{OH}{CH_2}-\underset{Br}{CH_2} \xrightarrow[-H_2O]{OH^-} \overset{O^-}{CH_2}-\underset{Br}{CH_2}$$

ethylene dibromide bromohydrin alcoxide



The reaction possibilities for ethylene dibromide do not stop here. In addition to the substitution reaction, elimination reactions are also possible under the hydrolysis conditions, yielding olefines:

$$Br\text{-}CH_2CH_2\text{-}Br \qquad \begin{matrix} CH_2{=}CH_2 + H_2O + 2\ Br^- \\ CH_2{=}CHBr + H_2O + Br^- \end{matrix}$$

The overall rate as well as the rates of the individual possible reactions will depend on the reaction conditions, especially the temperature. Table I shows the concentrations of EDB solutions in buffers of pH5, pH7, and pH9 from time zero to time 140 days, and Table II shows the percentages of initial concentration reacted at different times. It is evident from the figures of Table I that the rate of hydrolysis at 25°C is greater for pH5 and smaller for the pH9 solutions. This is contrary to the expectation of greater rates at higher pH values. At 45°C, however, the rates increase as the pH of the solution increases.

Figures I through VI represent the change in concentration of ethylene dibromide with time for all the 6 combinations of pH and temperatures. At 25°C and for all three pH solutions, the concentration decreases slowly and almost linearly with time. Such linear decrease in the concentration indicates an apparent zero order reaction.

It is very hard to accept a zero order reaction for a substance such as ethylene dibromide with so many possible decomposition pathways. At such low concentrations, however, an excess of buffer reagents and very mild conditions can result in an overall decrease in concentration independent of the concentration itself.

On the other hand, at 45°C and for all three pH solutions, the rate of hydrolysis is greater and the plots of concentration versus time do not yield a straight line. Under these conditions, the apparent order of the reaction is not zero.

Figures VII through XII represent plots of logC versus time. According to the theory described in the introduction, if such a plot produces a straight line, the reaction is of first order. Again, the plots for the solutions at 25°C and all three pHs are almost straight lines. It is not possible, of course, to have a reaction follow zero and first order kinetics at the same time. However, we may be dealing with a situation in which, under the experimental conditions, the rate is between zero and first order.

At 45°C, on the other hand, the plot of logC versus time approaches a straight line as the pH increases from 5 to 9, becoming a straight line at pH=9.

Again, according to the theory of reaction rates, this would be interpreted as a change of the apparent reaction order from zero to first as the temperature increases from 25°C to 45°C and as the pH increases from 5 to 9.

Another criterion for first order reactions is the constant values of k calculated from equation 7. at different times during the course of the reaction. Tables III through VIII show the values of the reaction rate constant during the progress of the hydrolysis reaction of EDB and for all the combinations of pH and temperature. For each solution, the values of k are not close as they would be expected to be for a true first order reaction. They are, however, of the same order of magnitude. The closest agreement of k values is for the hydrolysis reaction at 45°C and pH 9 (Table VII), for which the graph of logC versus time (Figure VI) also suggests a first order.

At the end of the 140-day incubation period, each sample was analyzed for bromide ion by ion chromatography and for volatile organic byproducts of EDB hydrolysis by GC/MS.

The results of the bromide analysis are shown in Table IX. It is interesting to note that at 140 days' incubation time, the percentages of EDB reacted are very similar to the corresponding percentages of total bromine content converted to bromide ion (comparison of Tables II and VI).

The analysis for volatile organic byproducts was done using a purge-and-trap module (Tekmar) interfaced with a Finnigan GC/MS (OWA-1000). The only product identified was ethylene bromide (CH2-CHBr). Its concentration could not be assayed due to losses of evaporation upon breaking the sample ampule and due to unknown trapping efficiency of the Tenax trap for ethylene bromide. It appears, however, to be the major byproduct, especially for the 45°C, pH9 sample. This is a good indication that the major decomposition reaction at 45°C and pH9 is the dehydrohalogenation, e.g.

$$CH_2Br\,CH_2Br \xrightarrow{OH^-} CH_2 = CHBr + Br^- + H_2O$$

The product of debromination, ethylene ($CH_2 = CH_2$), was not detected. It is possible, however, that this is due to poor trapping efficiency of the Tenax adsorbent for ethylene.

SUMMARY

This study indicates the following:

1. The rate of hydrolysis of EDB is very slow at 25°C and at pH 5, 7 or 9.
2. At 25°C the rate increases as the pH decreases from 9 to 5.
3. The apparent order of the hydrolysis reaction is zero at 25°C for all three pH's.
4. At 45°C the rate increases as the pH increases from 5 to 9.
5. The rates at 45° are several times faster than at 25° at all three pH's, and the kinetic order approaches one.
6. The half-lives of hydrolysis range from 531 days at 25° and pH9 to 169 days at 45° and pH9, assuming a zero order reaction, and from 3352 days at 25° and pH9 to 137 days at 45° and pH9.
7. The primary reaction of EDB decomposition appears to be the dehydrohalogenation, at least at 45° and pH9.

TABLE I

CONCENTRATIONS OF EDB SOLUTIONS IN BUFFERS OF pH 5, pH 7 AND pH 9 FROM TIME ZERO TO TIME 140 DAYS

	25°C (C in ppm)			45°C (C in ppm)		
Time (days)	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
0	95.6	88.8	85.1	95.6	88.8	85.1
30	94.6	88.1	84.4	81.4	75.4	71.2
60	90.8	91.1	84.5	67.5	68.6	60.9
95	88.0	86.2	83.4	62.7	61.1	50.4
140	83.0	85.5	89.8	63.5	58.0	49.8

CHEM4
TABLEI

TABLE II

PERCENTAGE OF INITIAL CONCENTRATION OF ETHYLENE DIBROMIDE REACTED AT DIFFERENT TIMES

	25°C (C in ppm)			45°C (C in ppm)		
Time (days)	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
0	0	0	0	0	0	0
30	1.05	0.79	0.82	14.85	15.09	16.33
60	5.02	-	0.71	29.39	22.75	28.44
95	7.95	2.93	2.00	34.41	31.19	40.78
140	13.18	3.72	-	33.58	34.68	41.48

CHEM4
TABLEII

TABLE III

VALUES OF K AND $t_{1/2}$ FOR THE HYDROLYSIS REACTION OF EDB AT 25° and pH=5

Time t (days)	Concentration C (ppm)	t_2-t_1 (days)	C_1/C_2	$\log C_1/C_2$	K	$t_{1/2}$ (days)
0	95.6	0	-	-	-	-
30	94.6	30	1.0106	0.0046	0.000353	1963
60	90.8	60	1.0529	0.0224	0.000860	806
95	88.0	95	1.0864	0.0360	0.000873	794
140	83.0	140	1.1518	0.0614	0.00101	686

CHEM4
TABLEIII

TABLE IV

VALUES OF K AND $t_{1/2}$ FOR THE HYDROLYSIS REACTION OF EDB AT 25° and pH=7

Time t (days)	Concentration C (ppm)	t_2-t_1 (days)	C_1/C_2	$\log C_1/C_2$	K	$t_{1/2}$ (days)
0	88.8	0	-	-	-	-
30	88.1	30	1.0079	0.0034	0.000264	2625
60	91.1	60	0.9748	0.0111	0.000426	1627
95	86.2	95	1.1072	0.0442	0.001070	648
140	85.5	140	1.0386	0.0164	0.000270	2567

CHEM4
TABLEIV

TABLE VI

VALUES OF K AND $t_{1/2}$ FOR THE HYDROLYSIS REACTION OF EDB AT 45° and pH=5

Time t (days)	Concentration C (ppm)	t_2-t_1 (days)	C_1/C_2	$\log C_1/C_2$	K	$t_{1/2}$ (days)
0	95.6	0	-	-	-	-
30	81.4	30	1.1744	0.0698	0.005360	129
60	67.5	60	1.4163	0.1511	0.005800	120
95	62.7	95	1.5247	0.1832	0.004440	156
140	63.5	140	1.5055	0.1777	0.002920	237

CHEM4
TABLEVI

TABLE VII

VALUES OF K AND $t_{1/2}$ FOR THE HYDROLYSIS REACTION OF EDB AT 45° and pH=7

Time t (days)	Concentration C (ppm)	t_2-t_1 (days)	C_1/C_2	$\log C_1/C_2$	K	$t_{1/2}$ (days)
0	88.8	0	-	-	-	-
30	75.4	30	1.1777	0.0710	0.005450	127
60	68.6	60	1.2945	0.1121	0.004300	161
95	61.1	95	1.4535	0.1623	0.003940	176
140	58.0	140	1.5310	0.1850	0.003040	228

CHEM4
TABLEVII

TABLE VIII

VALUES OF K AND $t_{1/2}$ FOR THE HYDROLYSIS REACTION OF EDB AT 45° and pH=9

Time t (days)	Concentration C (ppm)	t_2-t_1 (days)	C_1/C_2	$\log C_1/C_2$	K	$t_{1/2}$ (days)
0	85.1	0	-	-	-	-
30	71.2	30	1.1952	0.0774	0.005940	117
60	60.9	60	1.3974	0.1453	0.005580	124
95	50.4	95	1.6885	0.2275	0.005510	126
140	49.8	140	1.7088	0.2327	0.003830	181

CHEM4
TABLEVIII

TABLE IX

CONCENTRATIONS OF BROMINE REACTED AND CONVERTED TO BROMIDE ION FOR ALL SIX SOLUTIONS OF EDB AND IN 140 DAYS INCUBATION TIME

Conditions t°, pH	Concentration of EDB mg/liter	Bromine content mg/liter	Bromine reacted mg/liter	Bromine reacted %
25°, pH 5	95.6	81.4	4.5	5.5
25°, pH 7	88.8	75.6	4.0	5.3
25°, pH 9	85.1	72.4	4.5	6.2
45°, pH 5	95.6	81.4	23	28.3
45°, pH 7	88.8	75.6	32	36.0
45°, pH 9	85.1	72.4	27.5	38.0

CHEM4
TABLEIX

TABLE X

AVERAGE HALF-LIVES ASSUMING ZERO AND FIRST ORDER KINETICS

pH, t°	t 1/2 (days) assuming zero order reaction	t 1/2 days assuming first order reaction
5, 25°C	531	1062
7, 25°C	1883 5.29 yr.	1867
9, 25°C	3436	3352
5, 45°C	208	161
7, 45°C	202	173
9, 45°C	169	137

CHEM4
TABLEX

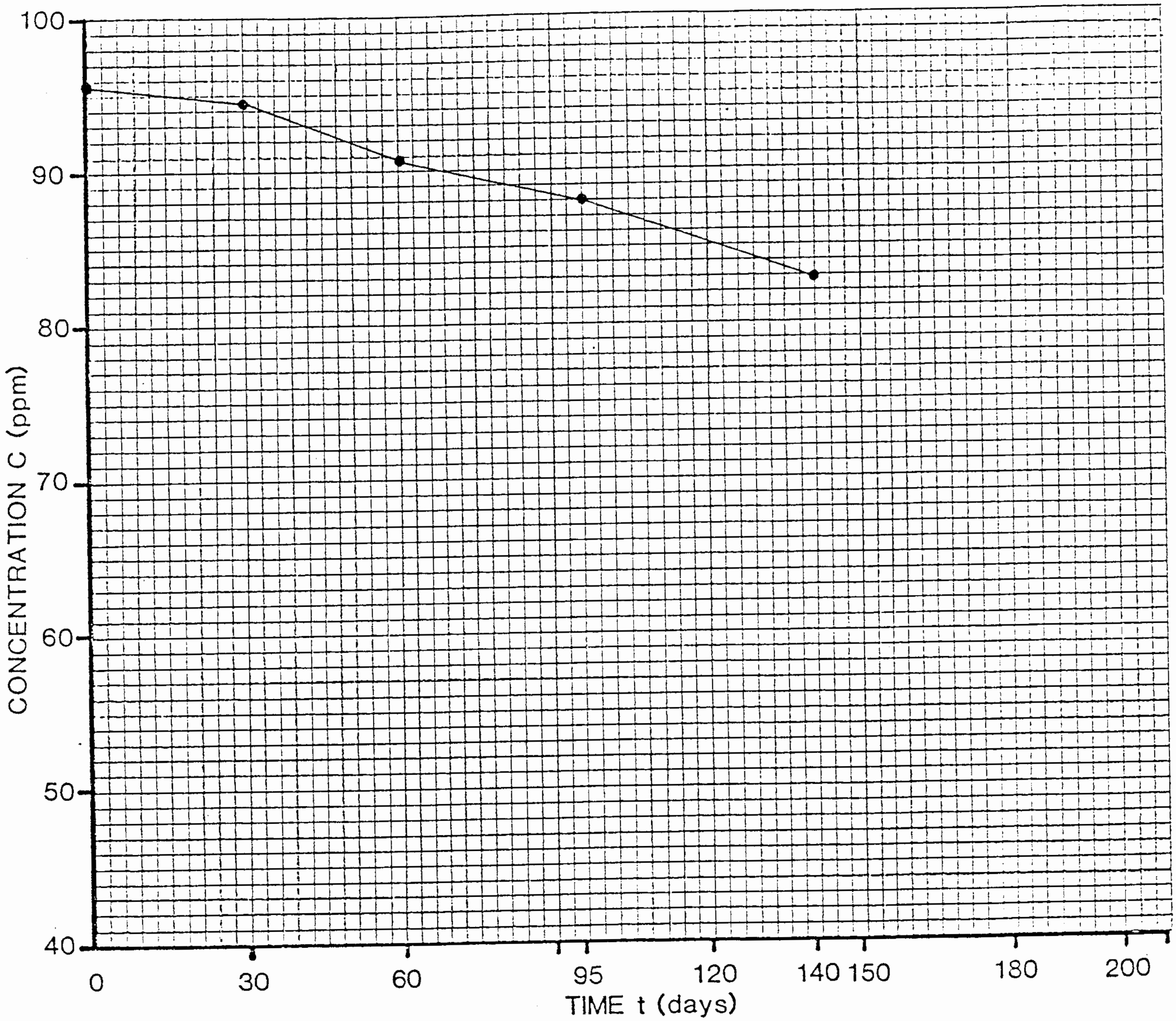


Figure I. Change in concentration of EDB with time at 25°C and pH = 5.

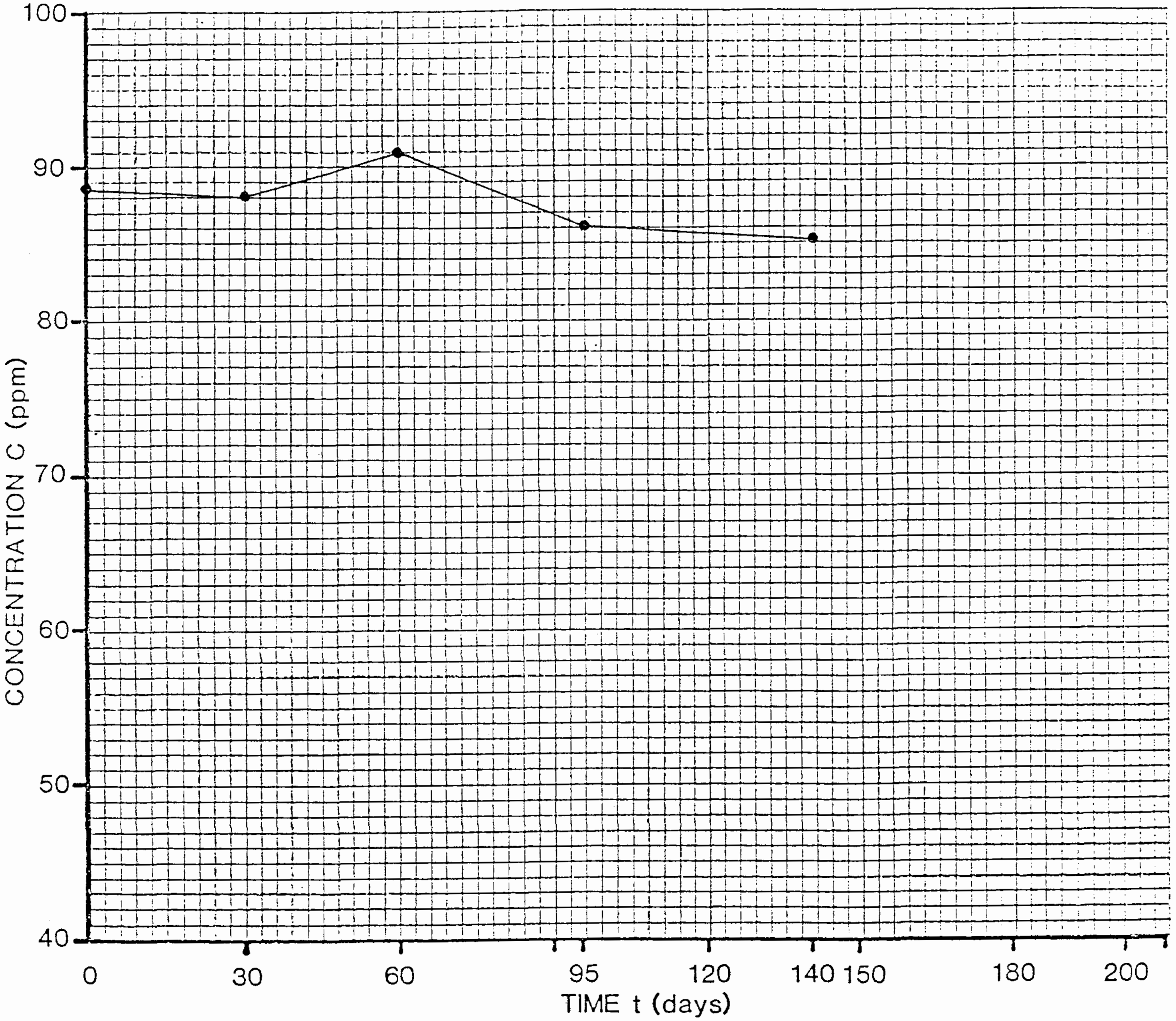


Figure II. Change in concentration of EDB with time at 25°C and pH = 7.

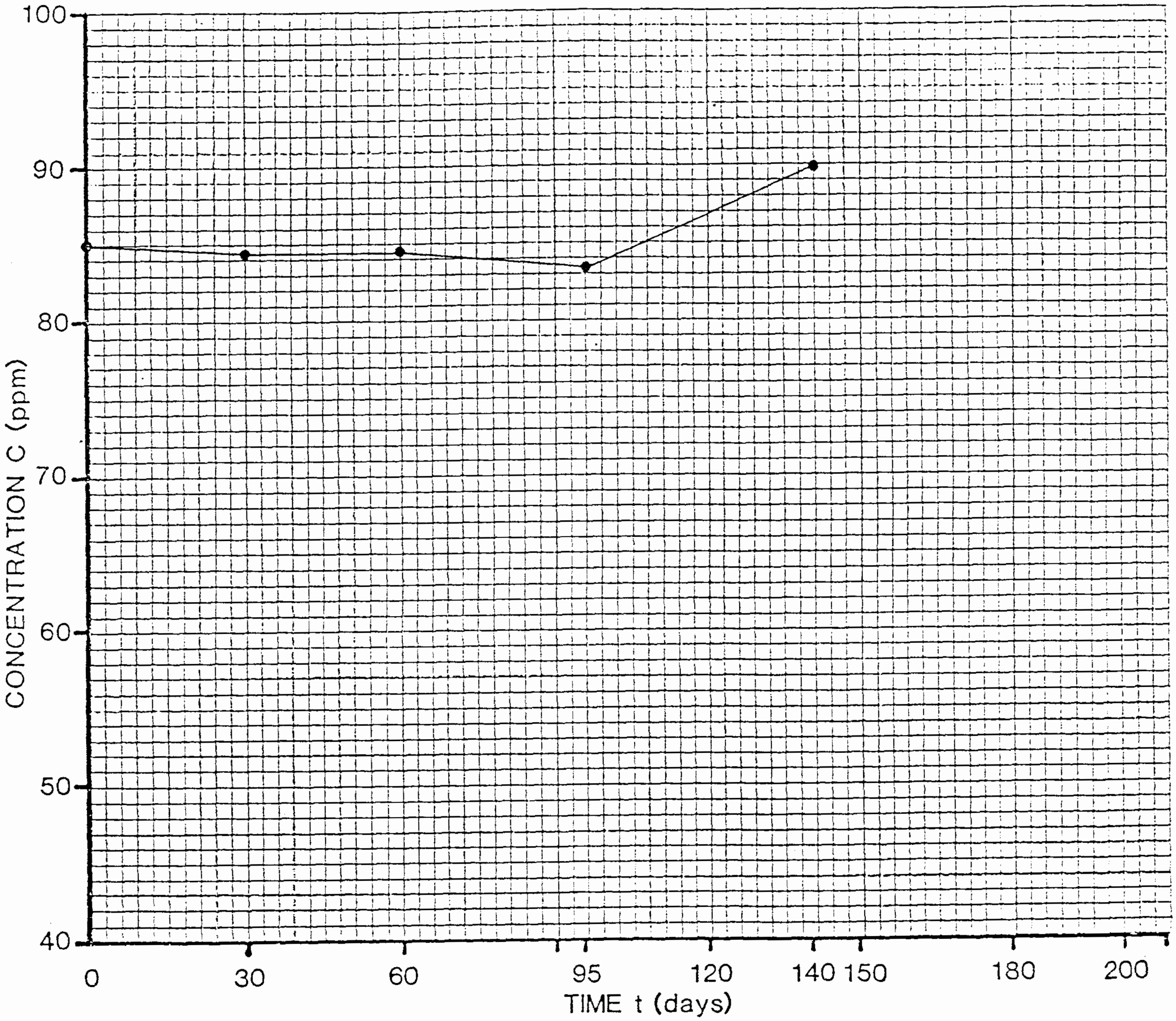


Figure III. Change in concentration of EDB with time at 25°C and pH = 9.

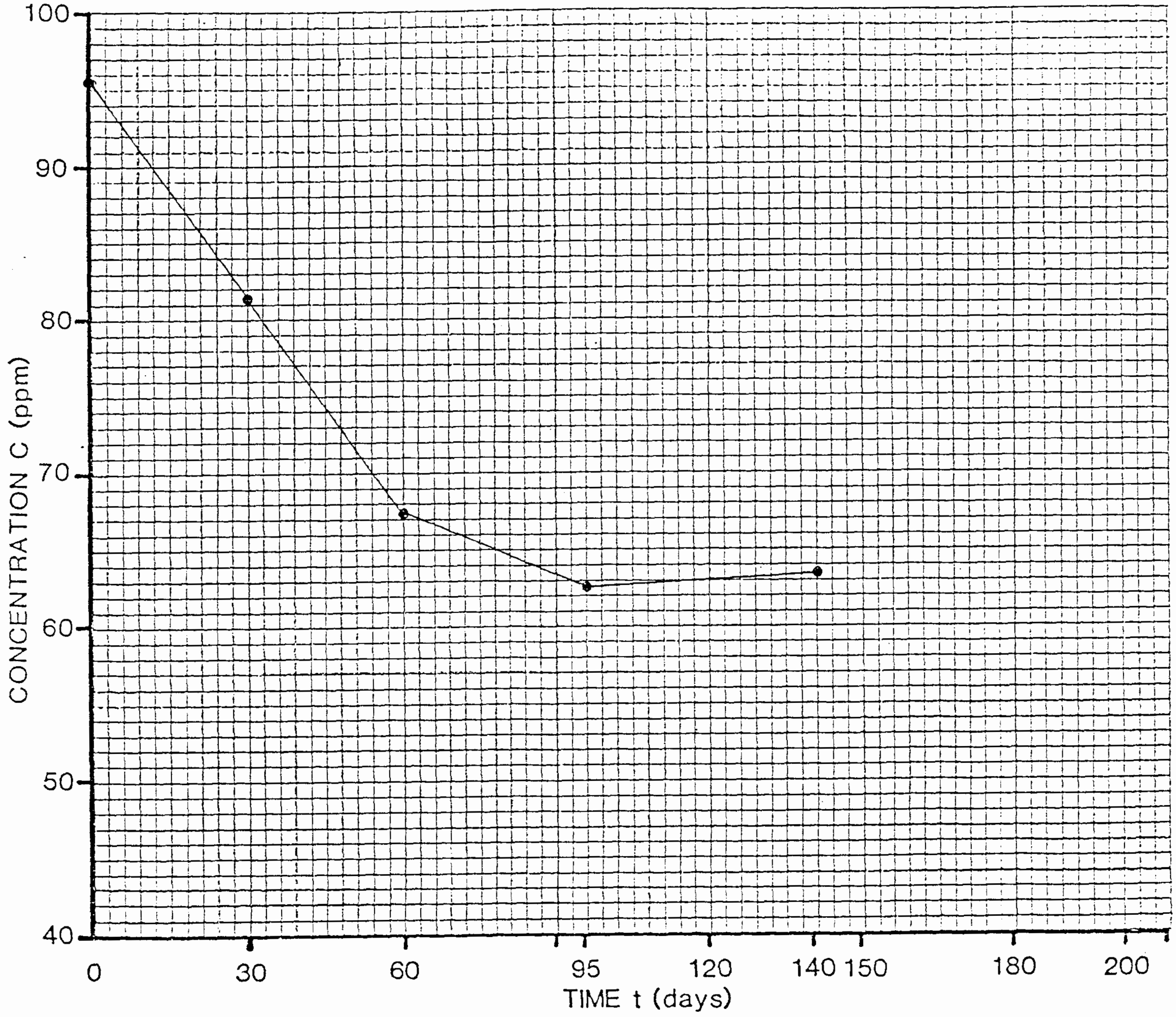


Figure IV. Change in concentration of EDB with time at 45°C and pH = 5.

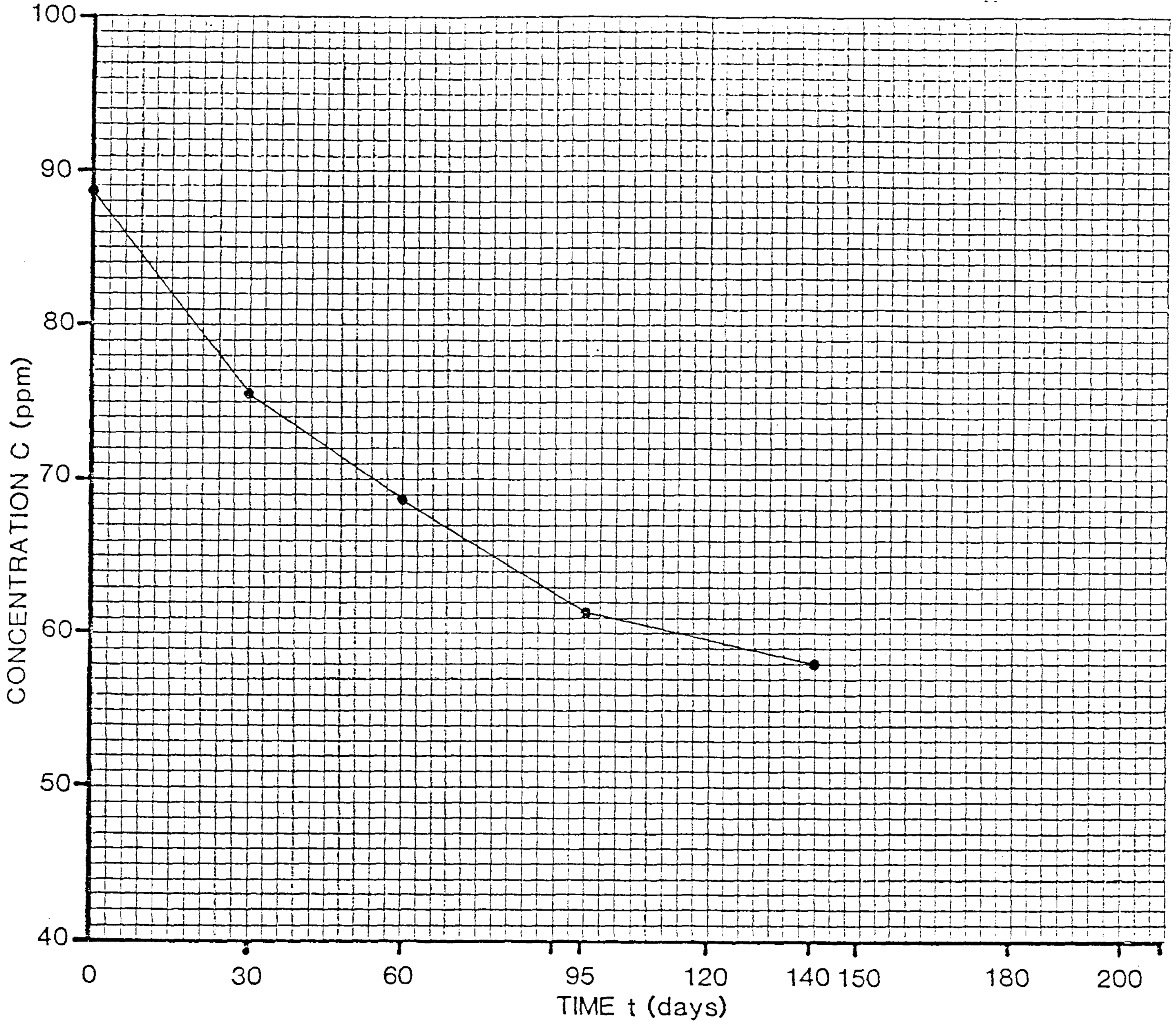


Figure V. Change in concentration of EDB with time at 45°C and pH = 7.

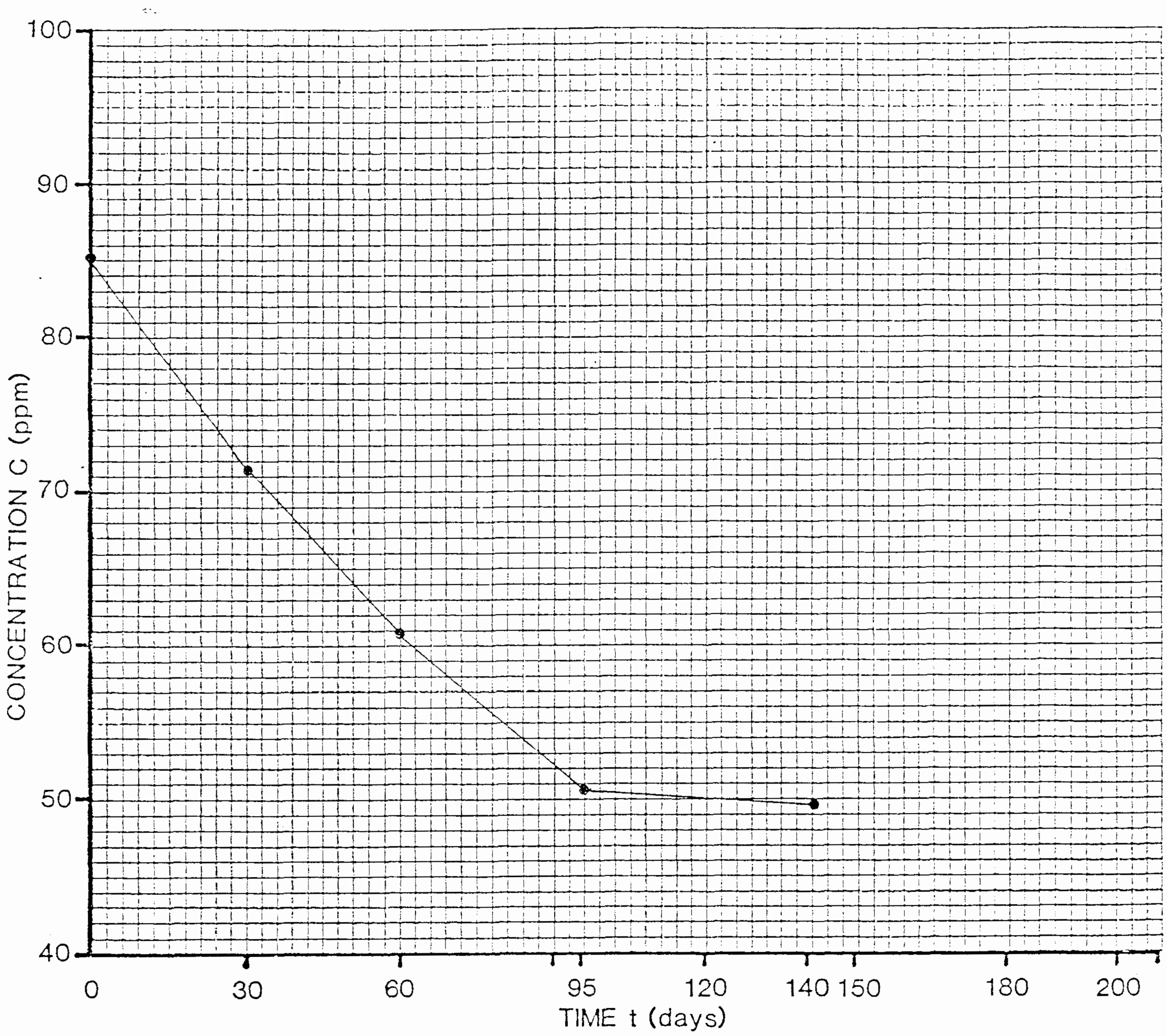


Figure VI. Change in concentration of EDB with time at 45°C and pH = 9.

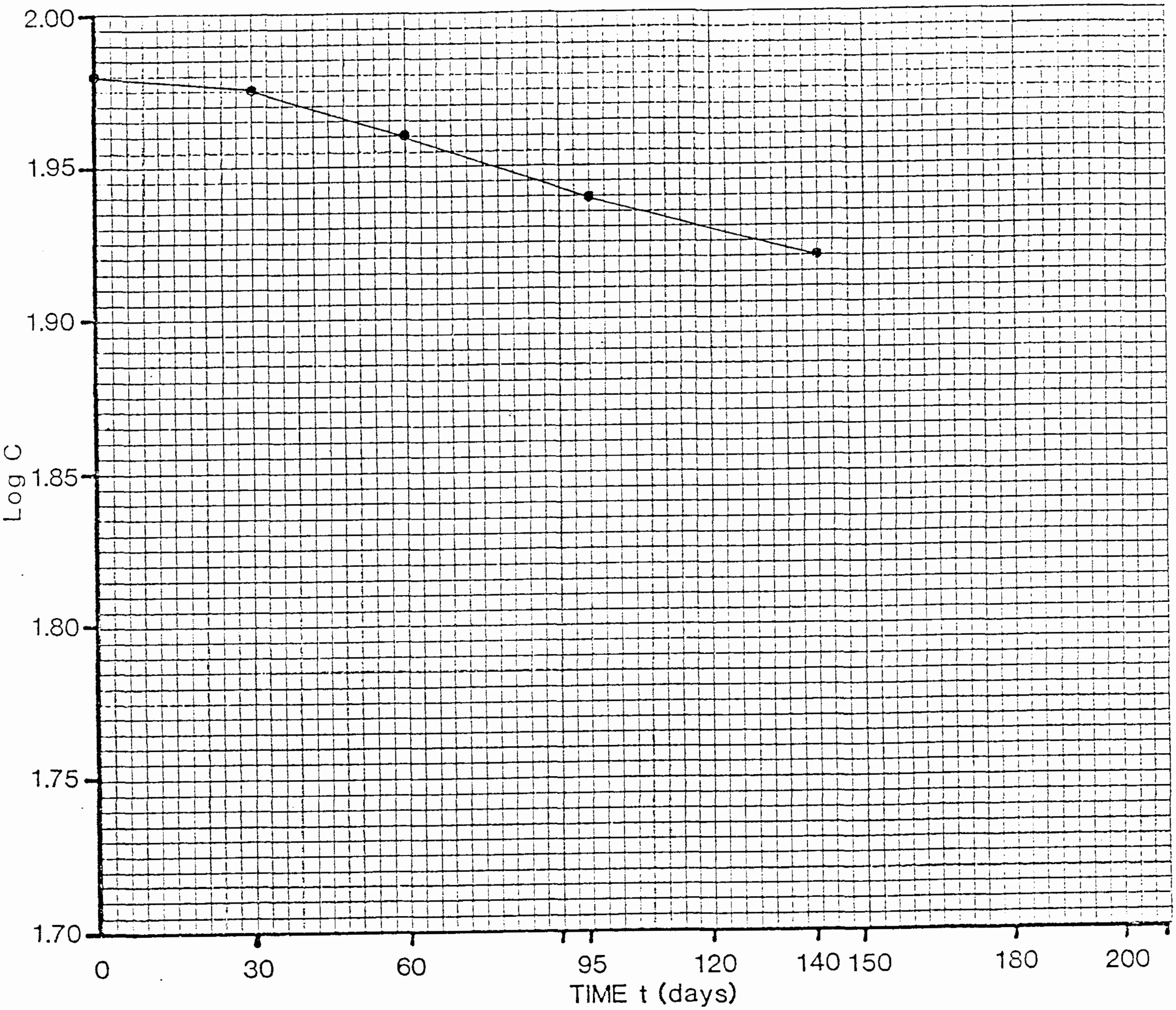


Figure VII. Plot of log C vs. time for the hydrolysis of EDB at 25°C and pH =5.

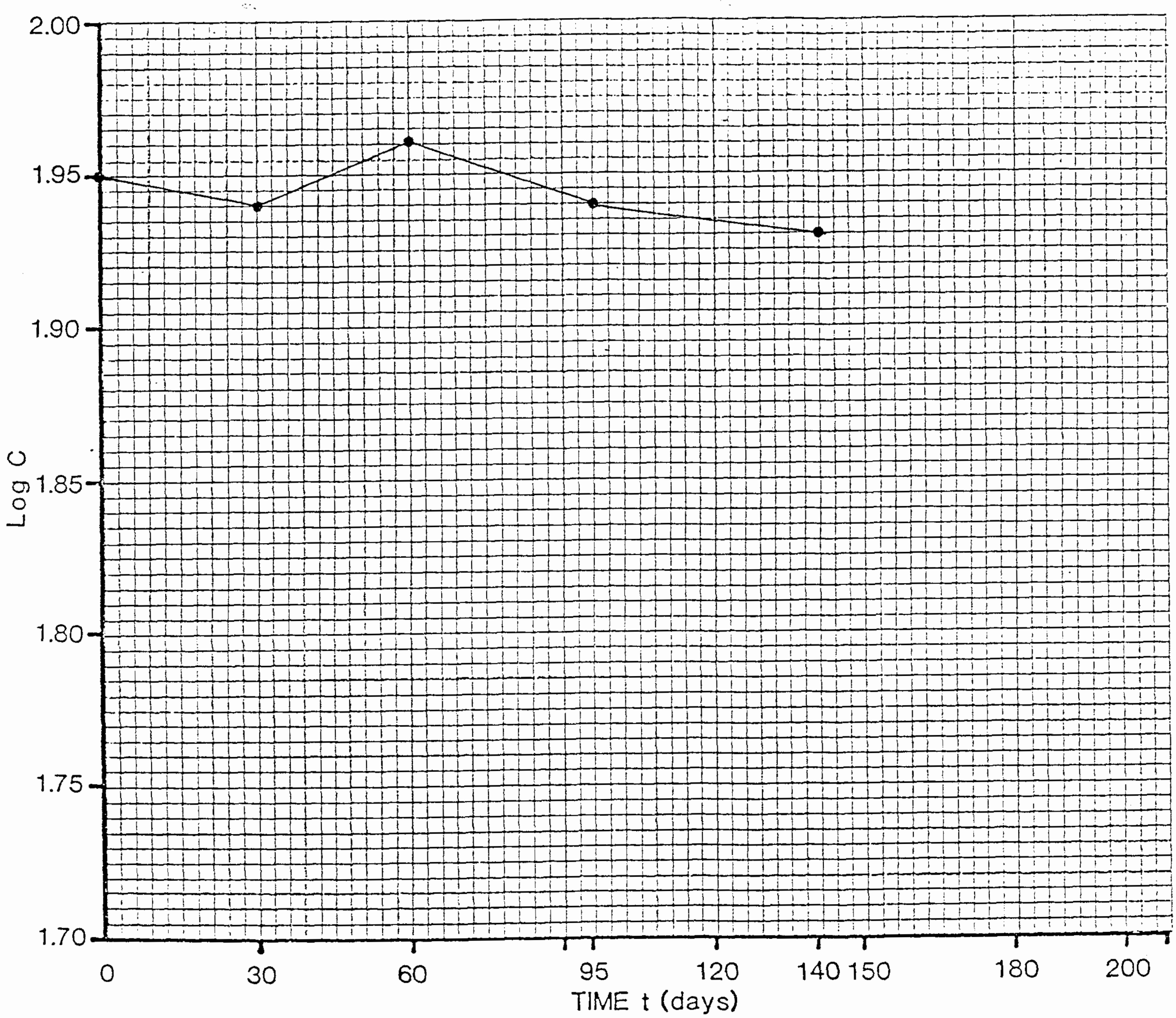


Figure VIII. Plot of log C vs. time for the hydrolysis of EDB at 25°C and pH = 7.

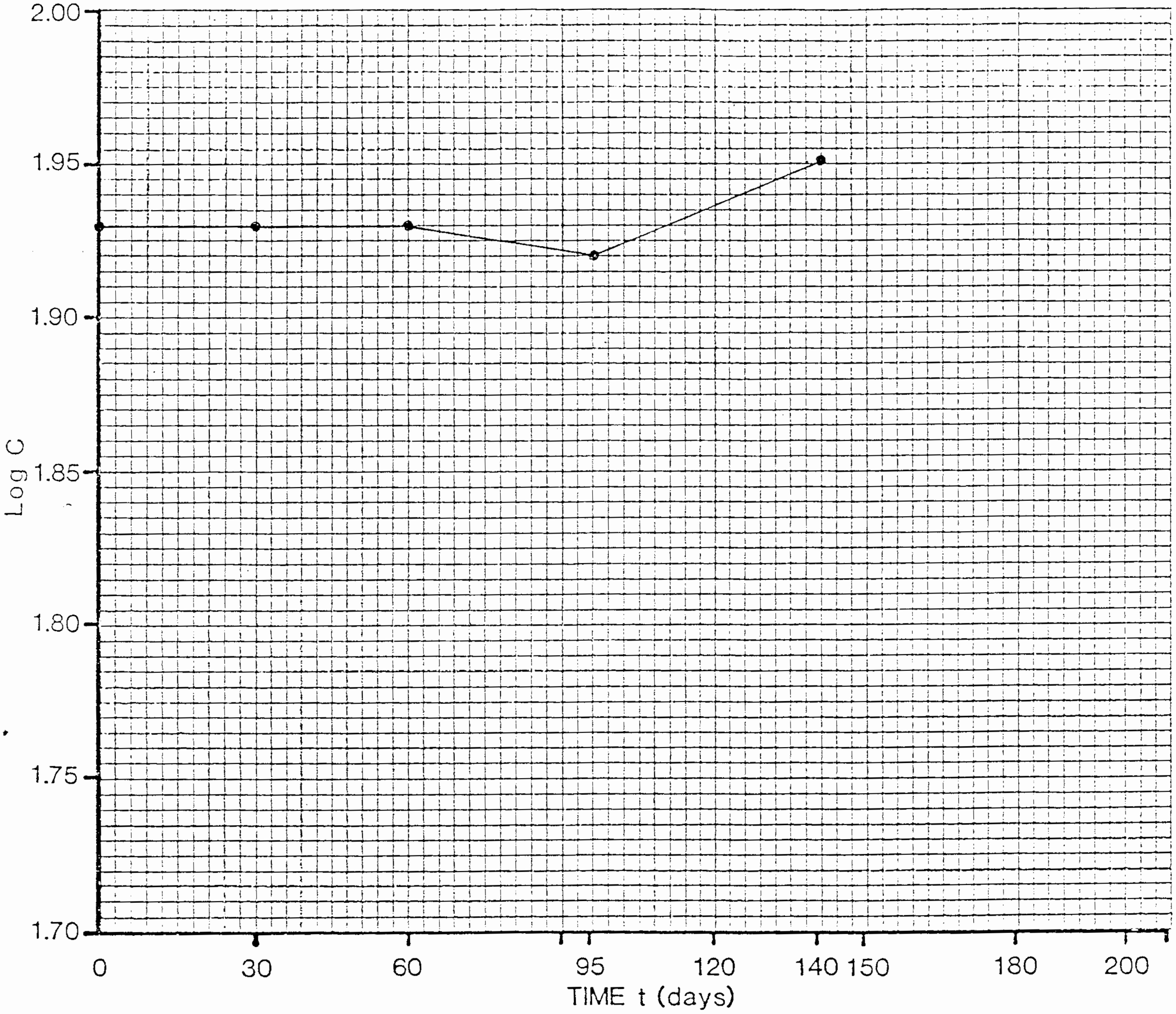


Figure IX. Plot of log C vs. time for the hydrolysis of EDB at 25°C and pH = 9.

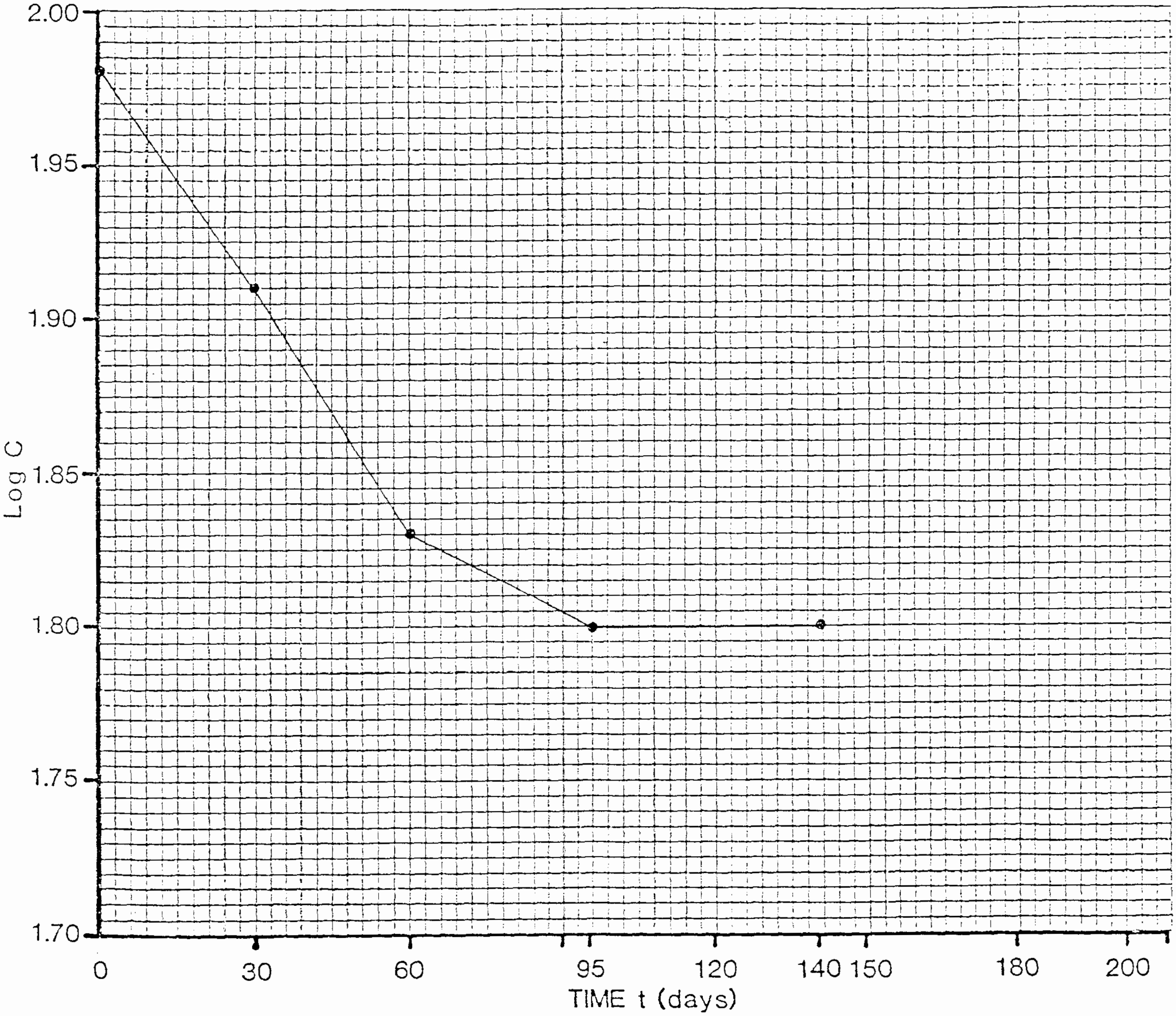


Figure X. Plot of log C vs. time for the hydrolysis of EDB at 45°C and pH = 5.

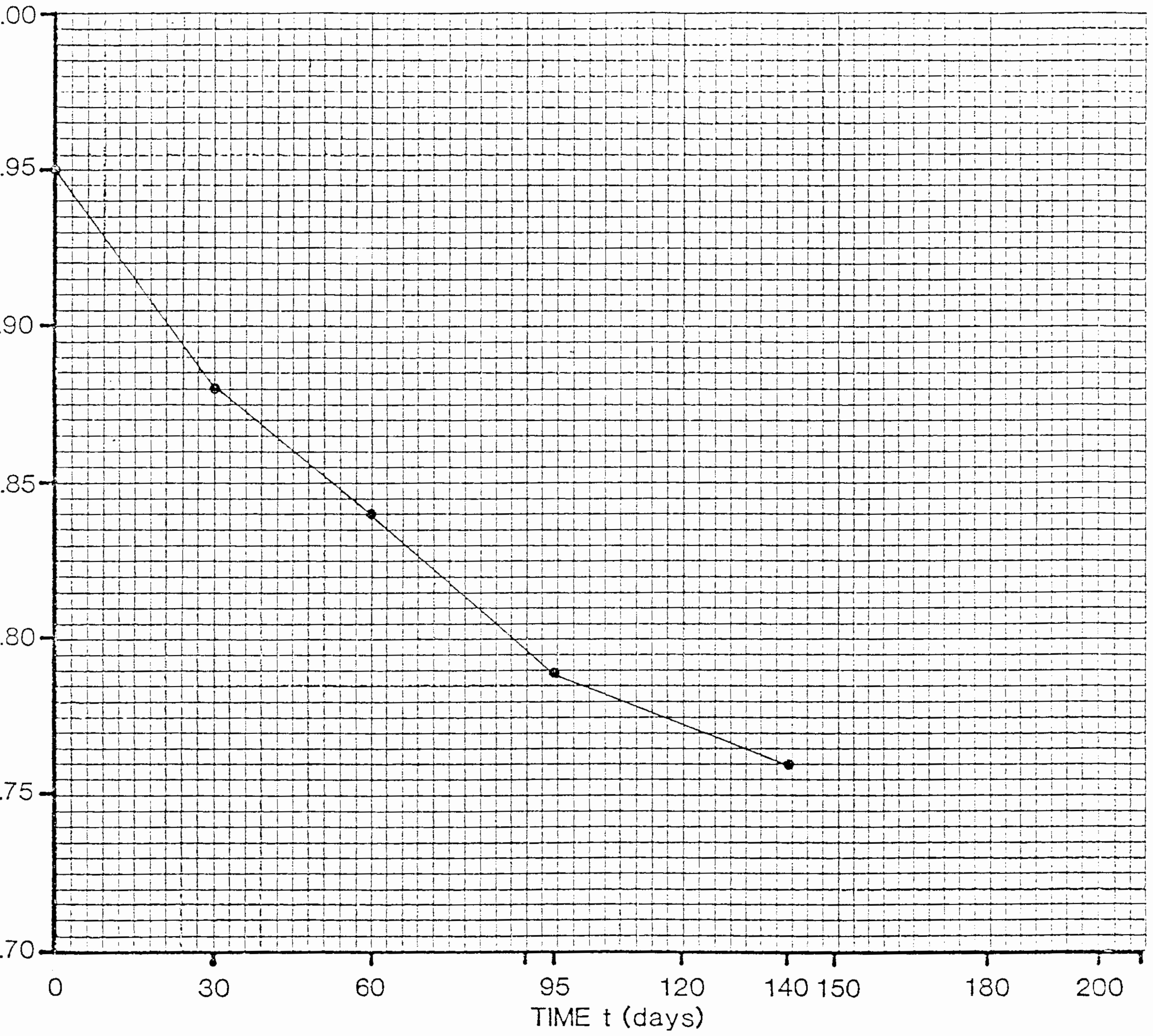


Figure XI. Plot of log C vs. time for the hydrolysis of EDB at 45°C and pH = 7.

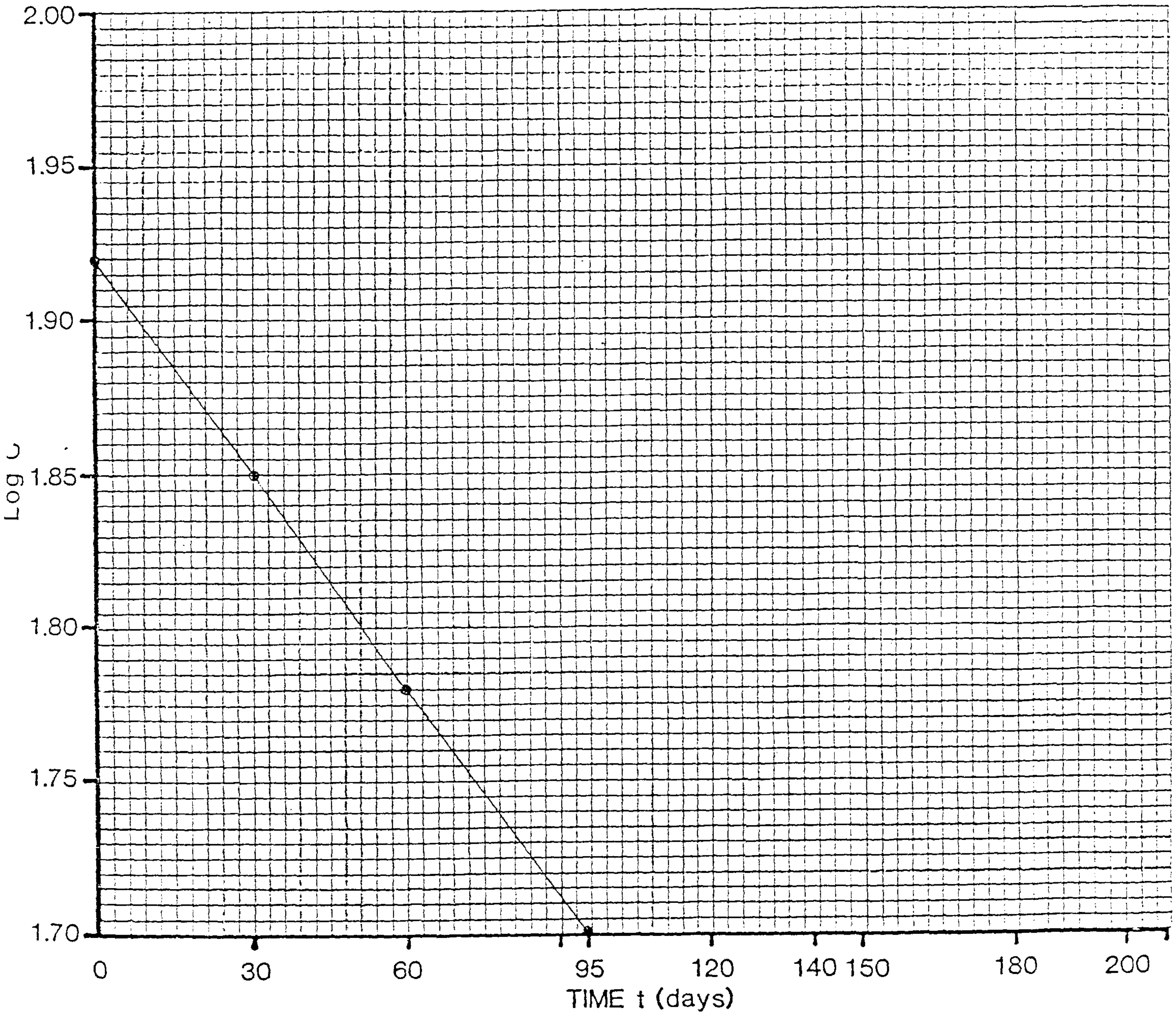


Figure XII. Plot of log C vs. time for the hydrolysis of EDB at 45°C and pH = 9.