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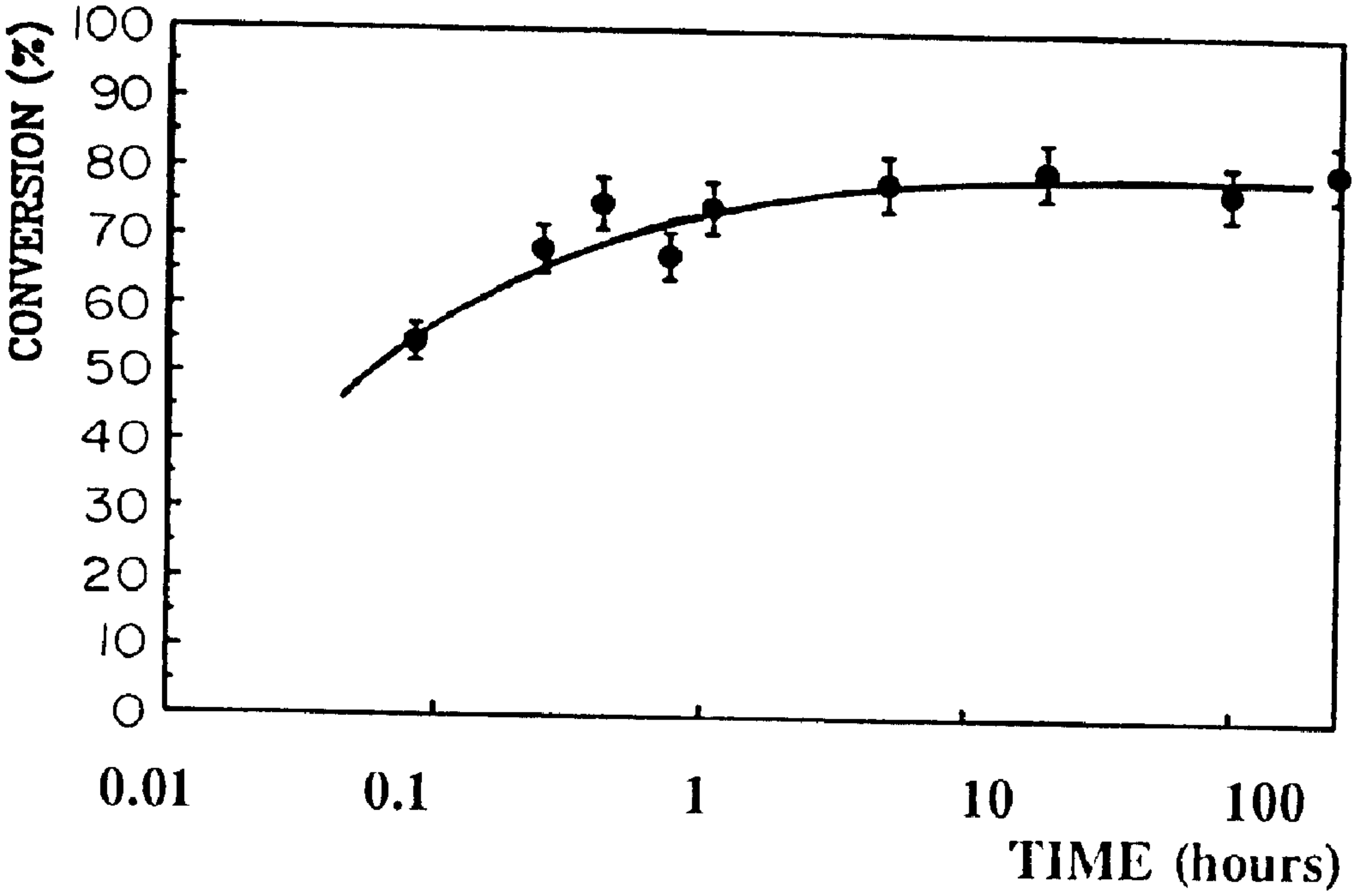
(54) **Titre** : CATALYSE DE CYCLOALCENES EN OLIGOMERES POLYCYCLIQUE SATURES
(54) **Title**: CATALYSIS OF CYCLOALKENES TO SATURATED POLYCYCLIC OLIGOMERS



(57) **Abrégé/Abstract**:

The invention relates to a homogeneous two-component catalyst system consisting of (a) a salt of a transition metal selected from the Group VIb of the Periodic Table; and (b) an organosilicon compound having the formula: $R_xSi(OR')_y(OSiR_3)_z$ (Ia) $(R_2SiO)_3$ (Ib) or $(R_3Si)_2NH$ (Ic) where R is identical or different and represents a hydrogen atom, a $C_1$-$C_4$ alkyl or phenyl group; R' represents a $C_1$-$C_4$ alkyl or phenyl group; $0 < x \leq 3$; $0 \leq y < 4$; z=0 or 1; $y+z \geq 1$; x+y+z=4; and wherein the molar ratio of component (b) to component (a) is at least about 0.5:1. Such a catalyst system is useful for the catalysis of cycloalkenes to saturated polycyclic oligomers.

# ABSTRACT

The invention relates to a homogeneous two-component catalyst system consisting of (a) a salt of a transition metal selected from the Group VIb of the Periodic Table; and (b) an organosilicon compound having the formula:

$$R_xSi(OR')_y(OSiR_3)_z \quad (Ia)$$

$$(R_2SiO)_3 \quad (Ib)$$

or

$$(R_3Si)_2NH \quad (Ic)$$

wherein R is identical or different and represents a hydrogen atom, a $C_1$-$C_4$ alkyl or phenyl group; R' represents a $C_1$-$C_4$ alkyl or phenyl group; $0 < x \leq 3$; $0 \leq y < 4$; $z=0$ or 1; $y+z \geq 1$; $x+y+z=4$; and wherein the molar ratio of component (b) to component (a) is at least about 0.5:1. Such a catalyst system is useful for the catalysis of cycloalkenes to saturated polycyclic oligomers.

# CATALYSIS OF CYCLOALKENES TO SATURATED POLYCYCLIC OLIGOMERS

This application is a division of Canadian patent application No. 2,180,725 filed on January 31, 1994 and relating to a catalyst system for the ring-opening polymerization of cycloalkenes to produce polyalkenamers as well as to a process for the production of polyalkenamers utilizing such a catalyst system. The present divisional application is directed to a catalyst system for the polymerization of cycloakenes to produce saturated polycyclic oligomers as well as to a process for the production of saturated polycyclic oligomers utilizing such a catalyst system.

Polyalkenamers play an important role in the rubber industry as they enter in the manufacture of synthetic rubbers. Some of these polymers are produced by a catalyzed ring-opening polymerization of cycloalkenes. The catalysts employed are generally two-component catalytic systems comprising a salt of a transition metal from Group VIb or VIIb of the Periodic Table and an organometallic compound of a metal from Groups Ia to IVa of the Periodic Table. The most common catalyst systems are based on tungsten or molybdenum salts, such as the well known system $WCl_6/Sn(CH_3)_4$. However, the ring-opening polymerization of cycloalkenes such as cyclooctene with this system may take from several days to several weeks to reach completion.

In order to accelerate the polymerization, it is known to add a third catalyst component containing oxygen, such as water or an alcohol. For instance, the use of ethanol as an accelerator with the catalyst system $WCl_6/C_2H_5AlCl_2$ for polymerizing cyclopentene in benzene has been reported by E. A. Ostead et al in Die Makromolekulare Chemie, Vol. 154 (1972), pages 21-34. The amount of ethanol added must be strictly controlled as too little ethanol does not provide the desired accelerating effect and the reaction is extremely slow. Too much ethanol, on the other hand, has been found to terminate the reaction and inhibit same so that the polymerization cannot be re-initiated.

It is therefore an object of the present invention to overcome the above drawbacks and to provide an improved catalyst system for the ring-opening polymerization of cycloalkenes, whereby to increase the rate of polymerization.

It is another object of the invention to provide a catalyst system which does not adversely affect the polymerization if an excess of the catalyst system is used.

According to one aspect of the invention, there is provided a homogeneous catalyst system for the ring-opening polymerization of cycloalkenes to produce polyalkenamers, comprising:

a) a salt of a transition metal selected from the Group VIb of the Periodic Table;

b) an organometallic compound of a metal selected from Groups IIIa and IVa of the Periodic Table; and

c) an organosilicon compound having the formula:

$$R_xSi(OR')_y(OSiR_3)_z \qquad (Ia)$$

$$(R_2SiO)_3 \qquad (Ib)$$

or

$$(R_3Si)_2NH \qquad (Ic)$$

wherein:

R is identical or different and represents a hydrogen atom, a $C_1$-$C_4$ alkyl or phenyl group;

R' represents a $C_1$-$C_4$ alkyl or phenyl group;

$0 < x \leq 3$;

$0 \leq y < 4$;

$z=0$ or $1$;

$y+z \geq 1$;

$x+y+z=4$;

with the proviso that x=1 and y=3 when z=0;
and wherein the molar ratio of component (c) to component (a) is at least about 0.5:1.

Applicant has found quite unexpectedly that organosilicon compounds of formula (Ia), (Ib) or (Ic) as defined above can be used to activate known two-component catalytic systems, such as the system $WCl_6/Sn(CH_3)_4$, thereby increasing the rate of polymerization of cycloalkenes. These organosilicon compounds may be used in excess relative to the other catalyst components without adversely affecting the polymerization.

The catalyst system of the invention is prepared by first reacting component (a) with component (b), and thereafter adding component (c). The reaction of the transition metal salt with the organometallic compound is known to generate a carbene ligand.

Representative examples of the transition metal salts which may be used as the first catalyst component (a) are tungsten and molybdenum halides, such as molybdenum trichloride, molybdenum tetrachloride, molybdenum pentachloride, tungsten dichloride, tungsten tetrachloride, tungsten pentachloride, tungsten hexachloride, molybdenum dibromide, molybdenum tribromide, molybdenum tetrabromide, tungsten dibromide, tungsten pentabromide, tungsten hexabromide, molybdenum hexafluoride, tungsten hexafluoride, tungsten diiodide and tungsten tetraiodide. It is usually preferred to employ tungsten hexachloride.

Representative examples of organometallic compounds useful as the second catalyst component (b) include aluminum and tin compounds. Representative of such compounds are trialkylaluminums such as trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisopropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum and the like; dialkylaluminum halides such as diethylaluminum chloride, di-n-propylaluminum chloride, diisobutylaluminum chloride, diethylaluminum bromide, diethylaluminum iodide, diethylaluminum fluoride and the like; alkylaluminum dihalides such as ethylaluminum dichloride, ethylaluminum dibromide, propylaluminum dichloride, isobutylaluminum dichloride, ethylaluminum diiodide and the like; and tetraalkyltins such as tetramethyltin, tetraethyltins, tetra-n-propyltin, tetra-n-butyltin, tetraisopropyltin, tetraisobutyltin, tetrahexyltin, tetraoctyltin and the like. It is usually preferred to employ tetramethyltin.

Examples of suitable organosiloxanes of formula (Ia) or (Ib) which may be used as the third catalyst component (c) include phenyltriethoxysiloxane, 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane and hexamethylcyclotrisiloxane. It is also possible to use an organosilazane of formula (Ic), such as 1,1,3,3-tetramethyldisilazane, 1,3-diphenyl-1,1,3,3-tetramethyldisilazane or hexamethyldisilazane.

The molar ratio of the organosilicon compound to the transition metal salt must be at least 0.5(±0.1):1, since at a lesser molar ratio the organosilicon compound does not have any substantial activating effect. Preferred molar ratios of components (a):(b):(c) are 1:2:2.3 and 1:2:4.7.

The ring-opening polymerization of cycloalkenes with the catalyst system of the invention is generally carried out at a temperature ranging from about 0° to about 160°C. At a temperature above 160°C, there is a tendency for the catalyst system to decompose. The polymerization can be carried out in bulk or in solution since the catalyst system is homogeneous and thus soluble in the monomer or solvent.

Applicant has also found quite unexpectedly that saturated polycyclic oligomers can be produced by conducting the polymerization of cycloalkenes in the presence of the above catalyst system, but containing no organometallic compound. It is believed that the polymerization proceeds through a mechanism different than ring-opening, such as a cationic mechanism. The saturated polycyclic oligomers produced are stable at high temperature and can thus be used as lubricants or release agents.

The present invention therefore provides, in another aspect thereof, a homogeneous catalyst system for the polymerization of cycloalkenes to produce saturated polycyclic oligomers, comprising:

a) a salt of a transition metal selected from the Group VIb of the Periodic Table; and

b) an organosilicon compound having the formula:

$$R_xSi(OR')_y(OSiR_3)_z \qquad (Ia)$$

$$(R_2SiO)_3 \qquad (Ib)$$

or

$$(R_3Si)_2NH \qquad (Ic)$$

wherein:

R is identical or different and represents a hydrogen atom, a $C_1$-$C_4$ alkyl or phenyl group;

R' represents a $C_1$-$C_4$ alkyl or phenyl group;

$0 < x \leq 3$;

$0 \leq y < 4$;

$z=0$ or $1$;

$y+z \geq 1$;

$x+y+z=4$;

and wherein the molar ratio of component (b) to component (a) is at least about 0.5:1.

Further features and advantages of the invention will become more readily apparent from the following non-limiting examples and the accompanying drawings, in which:

Figure 1 graphically illustrates the degree of conversion with time for the bulk polymerization of cyclooctene at 45.0°C catalyzed with $WCl_6/Sn(CH_3)_4$/HMDS having a molar ratio of 1:2:4.7, where HMDS represents hexamethyl-disiloxane;

Figure 2 graphically illustrates the degree of conversion with time for the bulk polymerization of cyclooctene at 103.3°C catalyzed with $WCl_6$/$Sn(CH_3)_4$/HMDS having a molar ratio of 1:2:4.7;

Figure 3 graphically illustrates the degree of conversion with time for the bulk polymerization of cyclooctene at 157.3°C catalyzed with $WCl_6$/$Sn(CH_3)_4$/HMDS having a molar ratio of 1:2:4.7;

Figure 4 graphically illustrates the relation between the molar ratio of HMDS:$WCl_6$ and l n t, where t is the time required to reach equilibrium;

Figure 5 graphically illustrates the relation between l n (HMDS/$WCl_6$) and l n t; and

Figure 6 which is on the same sheet of drawings as Fig. 3, graphically illustrates the degree of conversion with time for the bulk polymerization of cyclooctene at 100°C catalyzed with $WCl_6$/$Sn(CH_3)_4$/HMDS having a molar ratio of 1:2:0.01.

## EXAMPLE 1

The bulk polymerization of cyclooctene was carried out under dry argon in order to eliminate water and oxygen which react with $WCl_6$ and destroys its activity. The monomer (99% pure) was distilled and dried over calcium hydride for at least one hour prior to its use. $WCl_6$ 99.9% pure was kept under dry argon. $Sn(CH_3)_4$ 99% pure was used without further purification and kept under dry argon. Hexamethyldisiloxane (HMDS) 99% pure was also kept under dry argon.

For the polymerization, $WCl_6$ was transferred into a dry ampoule through a side arm and then closed with a septum. $Sn(CH_3)_4$ was added with a syringe through the septum. The mixture was cooled, the side arm sealed and removed. The mixture was warmed up to room temperature and allowed to react for about 20 seconds. Then the monomer containing 4.7 moles of HMDS was transferred into the ampoule, cooled down and the ampoule sealed off. The ampoule was plunged into water, five minutes being necessary for melting of the mixture. The ampoule was then shaken in order to ensure homogeneity of the mixture and placed in a thermoregulated bath set at a temperature of 45°C.

The polymerization was stopped by the addition of methanol. The polymer samples were analyzed through nuclear magnetic resonance, gel permeation chromatography and mass spectometry. The samples comprised high-molecular-weight unsaturated linear polymer and unsaturated oligomers. The proportion of oligomers varied with polymerization time. In this case, the proportion was very high (as high as 80%) in the first few minutes and decreased with time.

In the experiment, 3 g of cyclooctene were polymerized using 10 mg of $WCl_6$. The molar composition of the catalyst system $WCl_6/Sn(CH_3)_3$/HMDS was 1:2:4.7.

As shown in Figure 1, the degree of conversion is plotted against time for the polymerization at 45°C. After approximately 5 minutes (0.1 h), the % conversion reached 50%. The % conversion levelled off at about 80%. The conversion did not go higher due to the formation of a gel, the monomer being trapped in the gel, preventing higher conversion.

## EXAMPLE 2

The same polymerization as described in Example 1 was carried out at 103°C and 157°C. Figures 2 and 3 show the conversion against time. At these temperatures, the % conversion reached almost 100%. At 103°C, the conversion was approximately 65% after 3 min. and about 80% at 157°C after the same time.

## EXAMPLE 3

The bulk polymerization of cyclooctene was carried out between 100° and 115°C using the following organosilicon compounds as accelerators:

- phenyltriethoxysiloxane (PTEOS)
- 1,1,3,3-tetramethyldisiloxane (TMDS)
- hexamethyldisiloxane (HMDS)
- hexamethylcyclotrisiloxane (HMCTS)

- hexamethyldisilane (HMDSi)
- 1,1,3,3-tetramethyldisilazane (TMDZ)
- hexamethyldisilazane (HMDZ)
- heptamethyldisilazane (HPMDZ)

The molar composition of the catalyst system $WCl_6/Sn(CH_3)_4$/accelerator was 1:2:5.

The efficiency of the accelerators in activating the system $WCl_6/Sn(CH_3)_4$ and accelerating the rate of polymerization was obtained through comparison of the yield obtained after 8 hours. The following data were obtained:

| Accelerator | Yield (%) |
|---|---|
| TMDS | 100 |
| HMCTS | 88 |
| PTEOS | 67 |
| HMDS | 65 |
| HMDZ | 35 |
| TMDZ | 35 |
| HPMDZ | inactive |
| HMDSi | inactive |

Based on the above results, the following qualitative efficiency scale was obtained:

TMDS > HMCTS > PTEOS, HMDS >
HMDZ, TMDZ >> HPMDZ, HMDSi = 0

As it is apparent, the presence of a methyl group on the nitrogen atom in heptamethyldisilazane inactivates the compound. The absence of a Si-O bond in hexamethyldisilane has also the same effect. Thus, a Si-O or a Si-NH-Si bond must be present in order to form an accelerator.

**EXAMPLE 4**

Using the same technique as described in Example 1, the polymerization of norbornene was carried out in cyclohexane. The catalyst system used was $WCl_6/Sn(CH_3)_4$/HMDS with a molar ratio of 1:2:4.7. The monomer concentration was 1.88 g in 10.0 ml of cyclohexane. The amount of $WCl_6$ was 10 mg. At room temperature, the % conversion reached 95% in approximately two minutes. No oligomers were found and the molecular weight of the polymer produced was about $10^6$.

**EXEMPLE 5**

The polymerization of cyclopentene was carried out in benzene, in the same manner as described in Example 1. The polymerization temperature was 0°C. The catalyst system used was $WCl_6/Sn(CH_3)_4$/HMDS with a molar ratio of 1:2:2.3. The monomer concentration was 33% and the $WCl_6$ concentration was 10 mg in 6 ml of monomer-solvent mixture. Because of a monomer-polymer equilibrium in this system, the polymerization never reached completion. It is known that for the polymerization of cyclopentene at 0°C, the maximum yield is 70% conversion. In the present case, this was easily achieved within 24 hours. No oligomers are found and the molecular weight of the polymer produced was about $10^6$.

**EXAMPLE 6**

The bulk polymerization of cyclooctene at 160°C using the catalyst system $WCl_6$/HMDS with a molar ratio of 1:4.7 led to the formation of low-molecular-weight polymer ($< 10^3$). The polymer produced comprised a mixture of dimers, trimers and higher oligomers. The polymer yield was 50% and was made of saturated and unsaturated oligomers. The proportion of saturated polycyclic oligomer was about 80% and reached 90% upon repeating the experiment at 100°C.

**EXEMPLE 7**

The bulk polymerization of cyclooctene was carried out at 103°C in the same manner as described in Example 1, using the catalyst system $WCl_6/Sn(CH_3)_4$/HMDS. The $WCl_6/Sn(CH_3)_4$ molar ratio was 1:2. The HMDS/$WCl_6$ ratio was allowed to vary and the time required to obtain equilibrium, measured accordingly. The HMDS/$WCl_6$ ratio is plotted againt l n t (time in hours) in Figure 4. As shown in Figure 5, when l n (HMDS/$WCl_6$) is plotted against l n t, using the same data and interpolated values between 5.0 and 7.0 for l n t, then two straight lines are obtained with a break-up point corresponding to a molar ratio of HMDS/$WCl_6$ equal to 0.5 (± 0.1). This molar ratio is the minimum ratio at which the organosilicon compound provides a substantial activating effect on the polymerization.

## COMPARATIVE EXAMPLE

The polymerization described in Example 1 was repeated, but the proportion of HMDS was reduced to a molar ratio of HMDS/$WCl_6$ equal to 0.01. Figure 6 shows the % conversion with time in terms of days. This can be compared with Figure 2 which shows that for nearly the same temperature, the % conversion is about 65% within 5 minutes, using a HMDS/$WCl_6$ molar ratio equal to 4.7.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A homogeneous two-component catalyst system for the polymerization of cycloalkenes to produce saturated polycyclic oligomers, consisting of:

a) a salt of a transition metal selected from the Group VIb of the Periodic Table; and

b) an organosilicon compound having the formula:

$R_xSi(OR')_y(OSiR_3)_z$ (Ia)

$(R_2SiO)_3$ (Ib)

or $(R_3Si)_2NH$ (Ic)

wherein:

R is identical or different and represents a hydrogen atom, a $C_1$-$C_4$ alkyl or phenyl group;

R' represents a $C_1$-$C_4$ alkyl or phenyl group;

$0 < x \leq 3$;

$0 \leq y < 4$;

$z=0$ or 1;

$y+z \geq 1$;

$x+y+z=4$;

and wherein the molar ratio of component (b) to component (a) is at least about 0.5:1.

2. A catalyst system according to claim 1, wherein component (a) is a tungsten or molybdenum halide.

3. A catalyst system according to claim 2, wherein component (a) is tungsten hexachloride.

4. A catalyst system according to claim 1, wherein component (b) is an organosiloxane selected from the group consisting of phenyltriethoxysiloxane, 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane and hexamethylcyclotrisiloxane.

5. A catalyst system according to claim 4, wherein component (b) is hexamethyldi-siloxane.

6. A catalyst system according to claim 3, wherein component (b) is hexamethyldi-siloxane.

7. A catalyst system according to claim 6, wherein the molar ratio of components (a):(b) is 1:4.7.

8. A catalyst system according to claim 1, wherein component (b) is an organosilazane selected from the group consisting of 1,1,3,3-tetramethyldisilazane, 1,3-diphenyl-1,1,3,3-tetramethyldisilazane and hexamethyldisilazane.

9. A process for the production of saturated polycyclic oligomers by the polymerization of cycloalkenes, which comprises conducting the polymerization at a temperature ranging from about 100° to about 160°C in the presence of a homogeneous catalyst system comprising:

a) a salt of a transition metal selected from the Group VIb of the Periodic Table; and

b) an organosilicon compound having the formula:

$R_xSi(OR')_y(OSiR_3)_z$ (Ia)

$(R_2SiO)_3$ (Ib)

or $(R_3Si)_2NH$ (Ic)

wherein:

R is identical or different and represents a hydrogen atom, a $C_1$-$C_4$ alkyl or phenyl group;

R' represents a $C_1$-$C_4$ alkyl or phenyl group;

$0 < x \leq 3$;

$0 \leq y < 4$;

$z=0$ or 1;

$y+z \geq 1$;

$x+y+z=4$;

and wherein the molar ratio of component (b) to component (a) is at least about 0.5:1.

10. A process according to claim 9, wherein component (a) of said catalyst system is a tungsten or molybdenum halide.

11. A process according to claim 10, wherein component (a) of said catalyst system is tungsten hexachloride.

12. A process according to claim 9, wherein component (b) of said catalyst system is an organosiloxane selected from the group consisting of phenyltriethoxysiloxane, 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane and hexamethylcyclotrisiloxane.

13. A process according to claim 12, wherein component (b) of said catalyst system is hexamethyldisiloxane.

14. A process according to claim 11, wherein component (b) of said catalyst system is hexamethyldisiloxane.

15. A process according to claim 14, wherein the molar ratio of components (a) : (b) of said catalyst system is 1:4.7.

16. A process according to claim 9, wherein component (b) of said catalyst system is an organosilazane selected from the group consisting of 1,1,3,3-tetramethyldisilazane, 1,3-diphenyl-1,1,3,3-tetramethyldisilazane and hexamethyldisilazane.

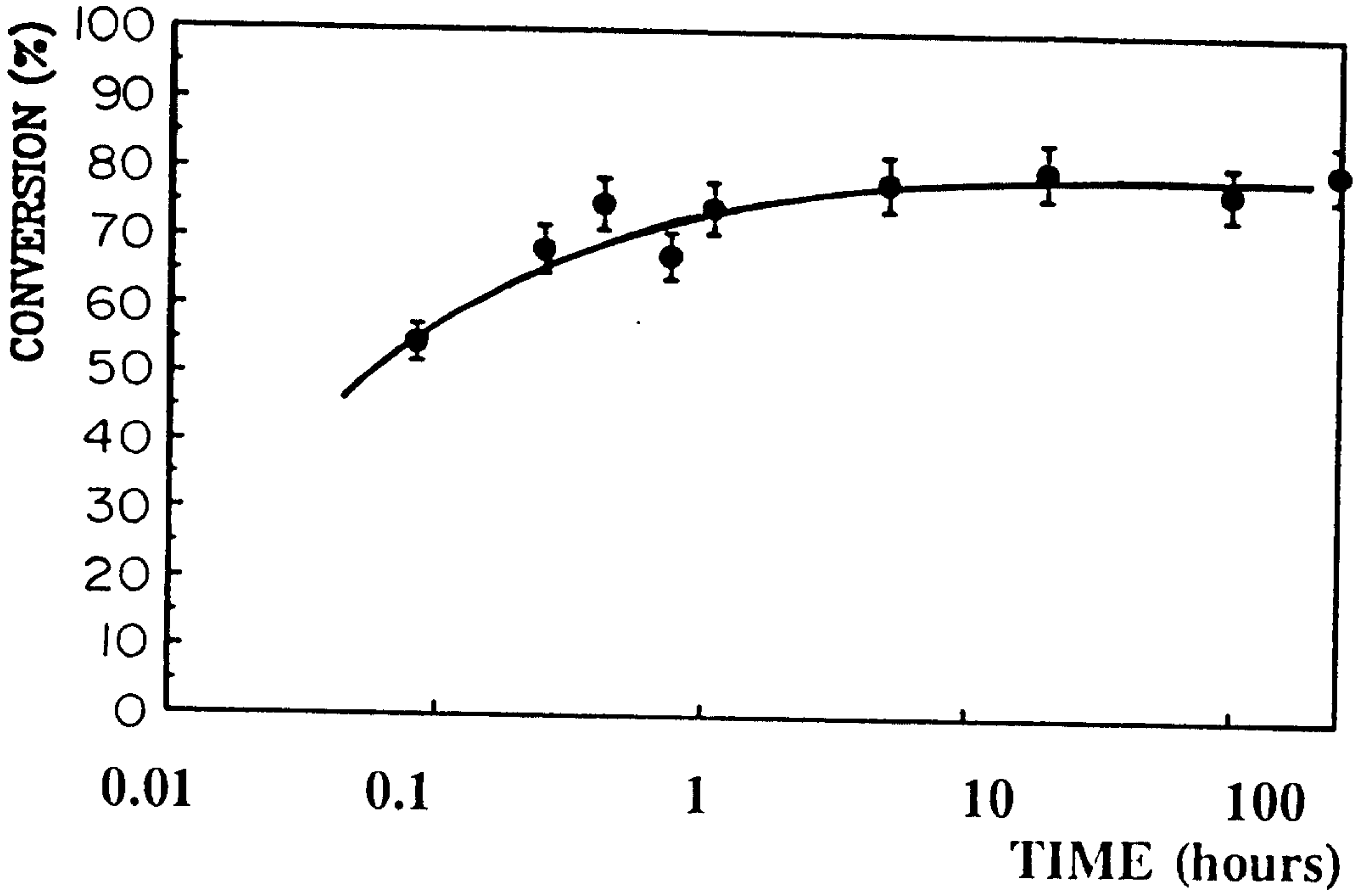
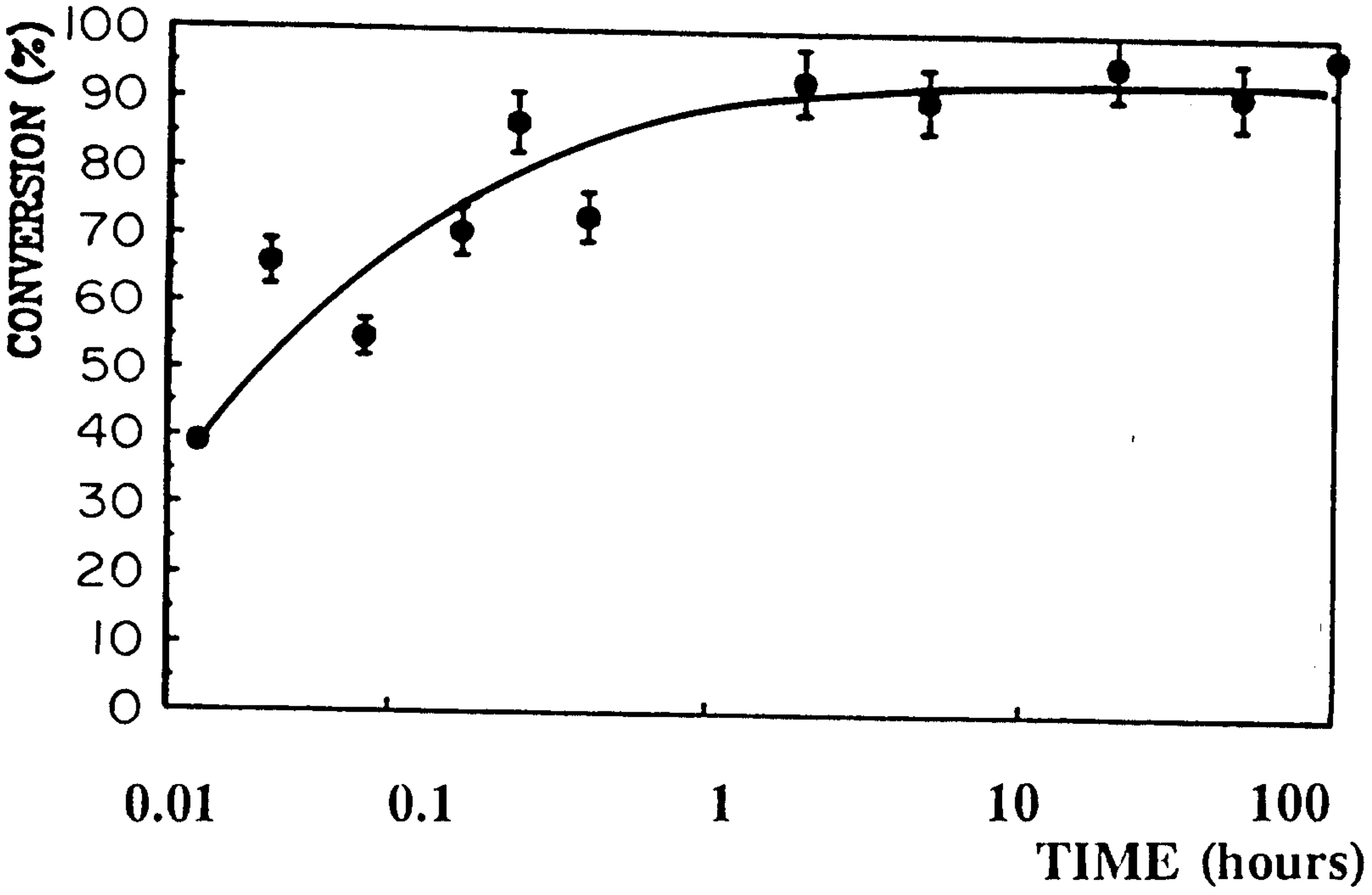

CONVERSION (%)
100
90
80
70
60
50
40
30
20
10
0
0.01
0.1
1
10
100
TIME (hours)

FIG. 1


CONVERSION (%)
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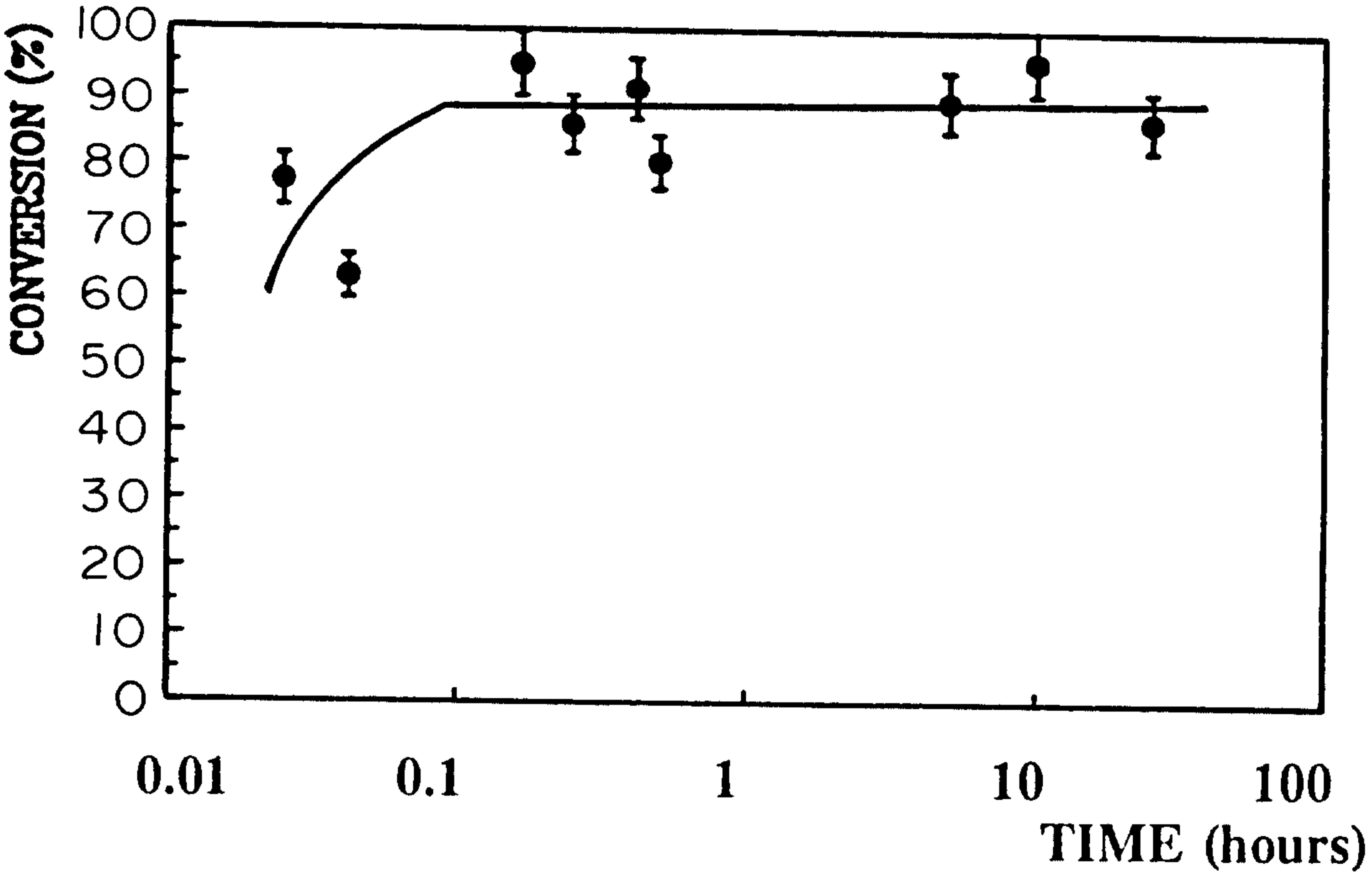
0.1
1
10
100
TIME (hours)

FIG. 2


CONVERSION (%)
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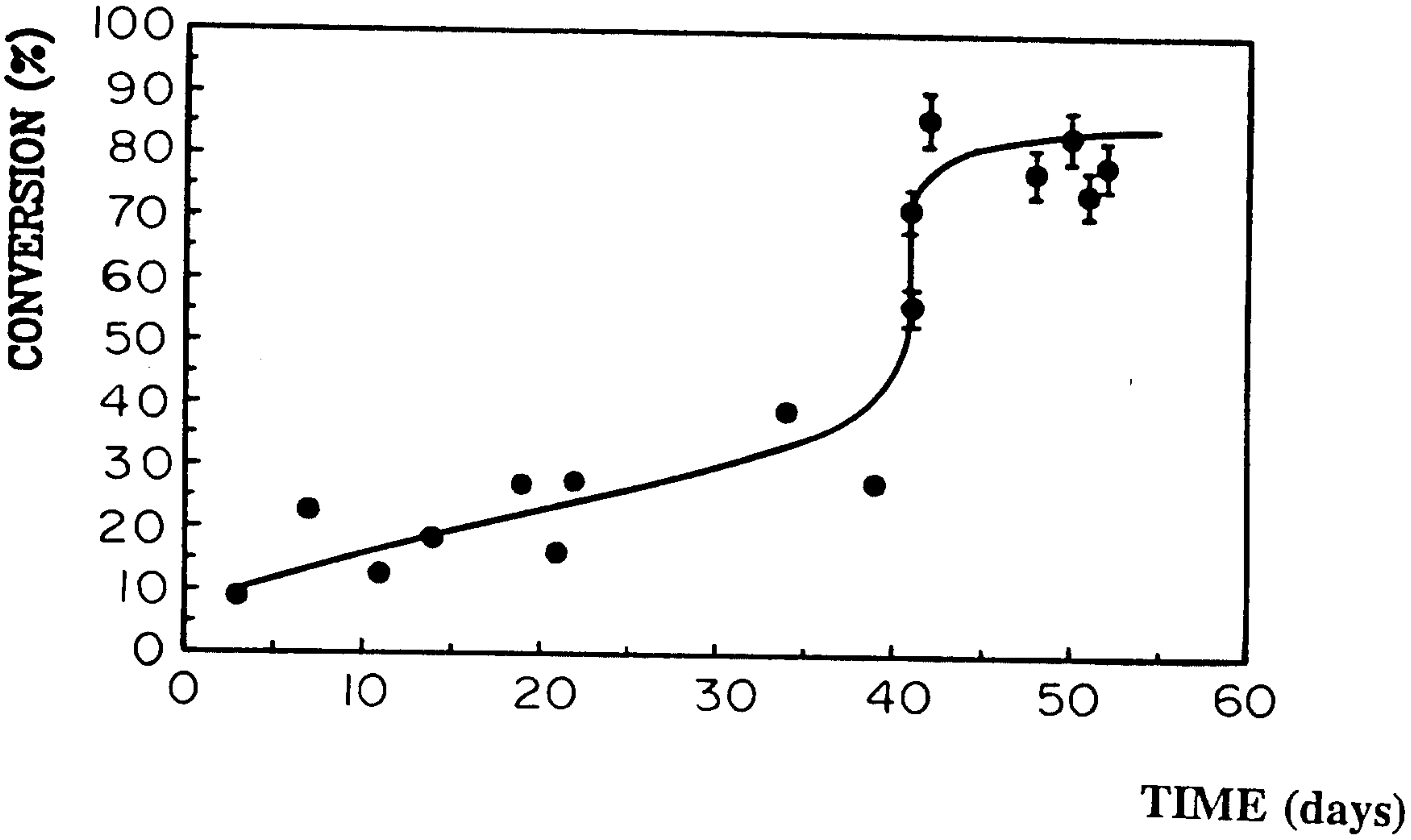
70
60
50
40
30
20
10
0
0.01
0.1
1
10
100
TIME (hours)

FIG. 3


CONVERSION (%)
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60
50
40
30
20
10
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0
10
20
30
40
50
60
TIME (days)

FIG. 6

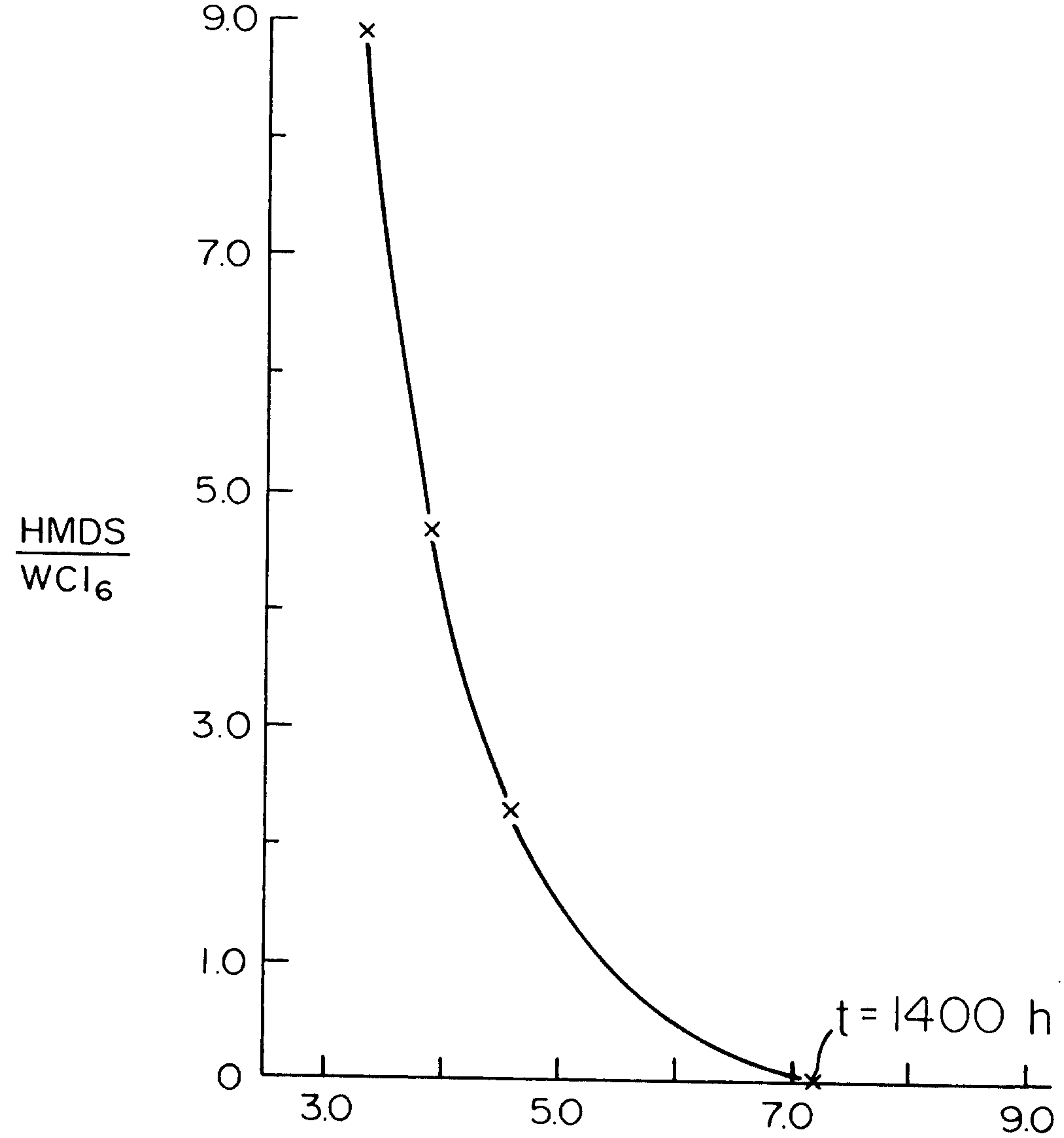


FIG. 4 ln t (t = hrs)

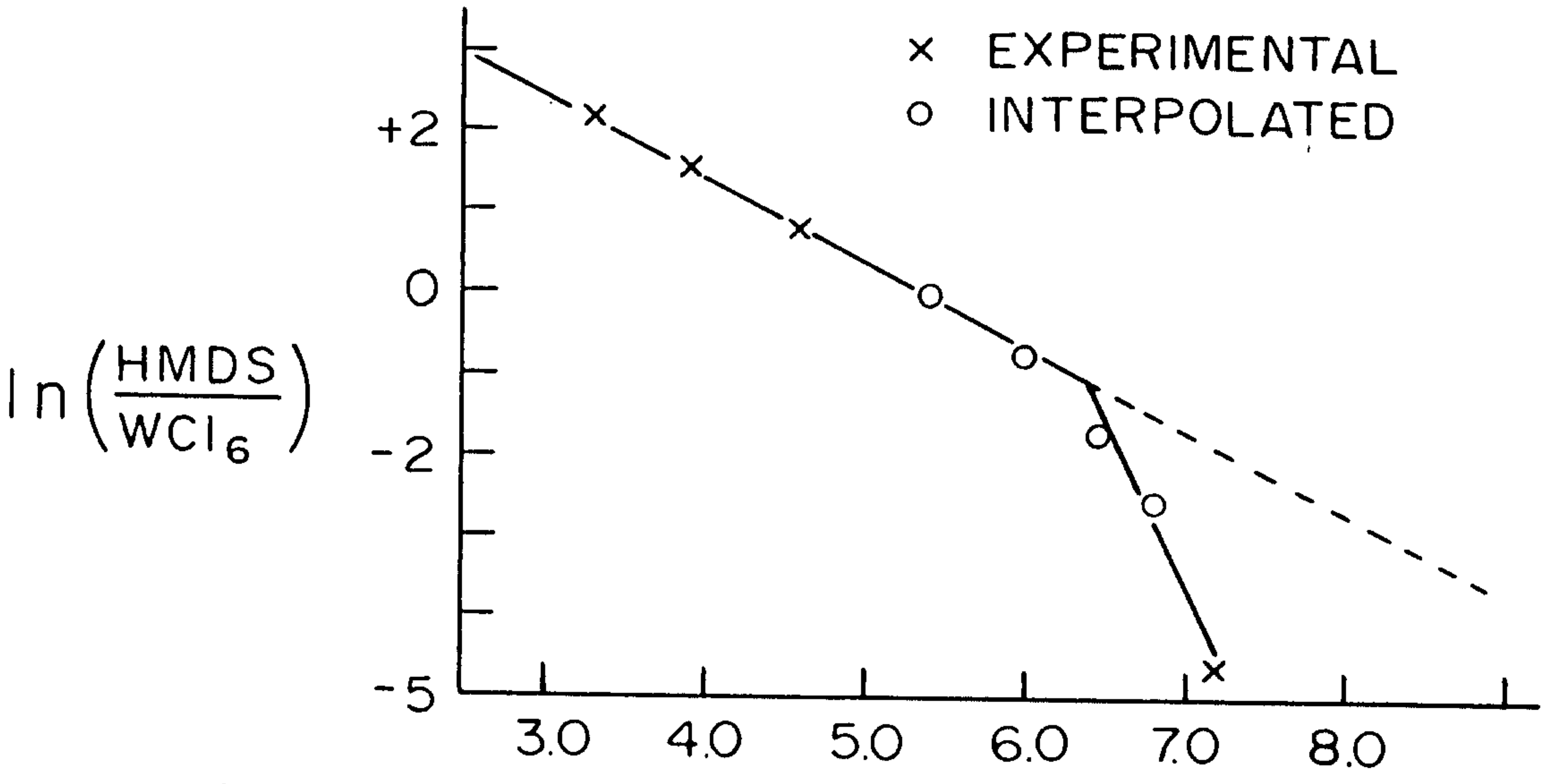
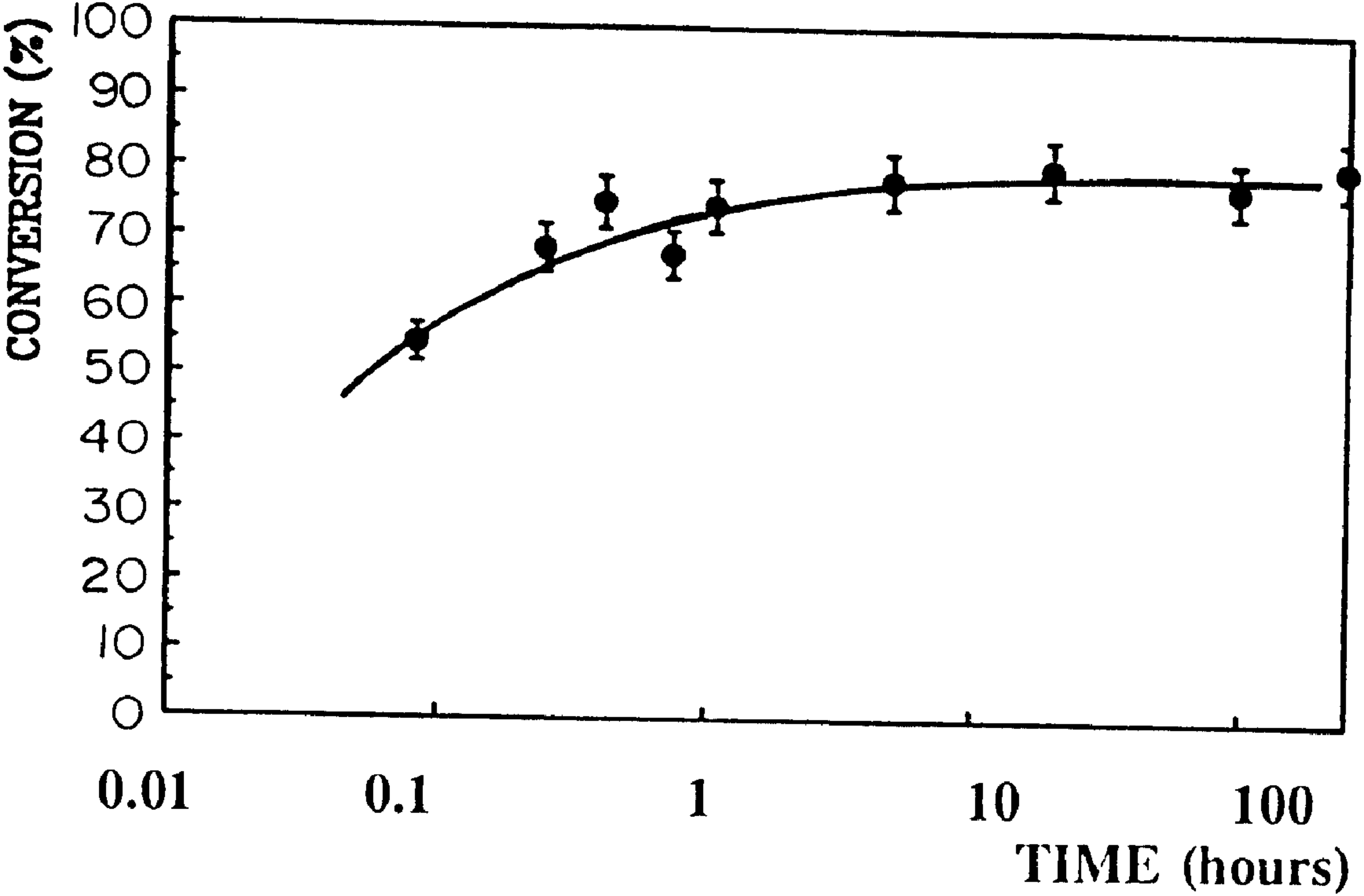


FIG. 5 ln t (t = hrs)


CONVERSION (%)
100
90
80
70
60
50
40
30
20
10
0
0.01
0.1
1
10
100
TIME (hours)