Elementary Reactions of Metal Alkyl in Anionic Polymerizations. V. Reaction of Di-n-butylzinc and Tri-n-butylaluminum witna α, β-Unsaturated Ketones

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Elementary Reactions of Metal Alkyl in Anionic Polymerizations. V. Reaction of Di-n-butylzinc and Tri-n-butylaluminum with α, β-Unsaturated Ketones

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SUMMARY

The reactions of n-Bu$_2$Zn and n-Bu$_3$Al with α, β-unsaturated ketones were studied. The elementary reactions were found to be conjugate addition and hydrogen abstraction reactions. One n-butyl group of metal alkyl was consumed in the conjugate addition, in contrast to the hydrogen abstraction reaction, all n-butyl groups being consumed in the latter elementary reaction. Conjugate addition rate constants were calculated regarding the conjugate addition as a second-order reaction with metal alkyl. On the basis of the kinetic data, infrared spectra of the reaction system, and the relative reactivity of the homologous vinyl ketones (α-methyl-substituted > unsubstituted > β-methyl-substituted), a four-centred mechanism was presented for the conjugate addition reaction of the metal alkyl with α, β-unsaturated ketone.

INTRODUCTION

In previous papers I-IV [1-4], the reaction modes of n-BuLi and n-BuMgBr with α, β-unsaturated carbonyl compounds and their relative reactivities were discussed. In addition, methyl vinyl ketone was found to be polymerized to give a highly stereoregular polymer by ZnR$_2$ or AlR$_3$ catalyst [5]. So, it is desirable, in order to elucidate the mechanism of anionic polymerizations, to investigate the reaction of ZnR$_2$ or AlR$_3$ with α, β-unsaturated ketones including

methyl vinyl ketone. In this paper the reaction mechanism of these metal alkyls with α, β-unsaturated ketones is discussed mainly in the light of a kinetic study.

EXPERIMENTAL

Reagents

Benzene was distilled over sodium wire-benzophenone. Tetrahydrofuran was distilled over potassium hydroxide, and again over sodium wire-benzophenone. Methyl isopropenyl ketone (MIPK) was prepared according to the literature [6] from methyl ethyl ketone and paraformaldehyde. Methyl vinyl ketone (MVK) was synthetized from acetone and paraformaldehyde by the same method used for MIPK. Methyl n-propenyl ketone (MNPK) was prepared according to the literature [7] from acetone and acetaldehyde. Benzalacetophenone (chalcone) was synthetized according to the literature [8] from benzaldehyde and acetophenone, and purified by recrystallization from cold petroleum-ether. Mesityloxide was purified by distillation. Acetone, methyl ethyl ketone, acetophenone, and benzaldehyde were purified by the usual method [9]. Methyl n-hexyl ketone was purified by distillation. Methyl n-butyl vinyl carbinol (MBVC) was synthetized from vinyl magnesium chloride and methyl n-butyl ketone in tetrahydrofuran according to the literature [10]. The purity of the reagents was checked by VPC (vapor phase chromatography). Nitrogen gas was purified by the same method described in a previous paper [4]. Di-n-butylzinc [11] and tri-n-butylaluminum [12] were prepared according to the literature and distilled under reduced pressure. Analyses of metal alkyls were performed by NMR, chelate titration, and VPC, determining the number of alkyl groups bonded to the metal.

Procedure

Benzene solution (0.15 mole/liter) of n-Bu_2Zn or n-Bu_3Al was prepared by diluting n-Bu_2Zn or n-Bu_3Al with benzene. The n-Bu_2Zn or n-Bu_3Al solution was added from a buret into a solution of α, β-unsaturated ketone with stirring under nitrogen atmosphere. After a given time interval, the reaction was stopped with excess acetic acid, and the amounts of reaction products were determined by VPC, packed with Silicone DC 550 and Poly(ethylene glycol) 20 M (2:1).

RESULTS

### Reaction Modes of n-Bu_2Zn with α, β-Unsaturated Ketone

In the reaction between n-Bu_2Zn and α, β-unsaturated ketones at 30°C, it was concluded that neither carbonyl reduction nor car-

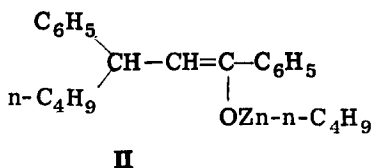bonyl addition takes place. This conclusion is based upon the
following results.

In a reaction with mesityloxide, n-butane from n-butyl groups
of $n\text{-}Bu_2Zn$ was quantitatively recovered, irrespective of the reac-
tion time, after stopping the reaction with excess acetic acid. Con-
trary to this, no n-butane was recovered from the reaction mixture
(reaction time, 24 hr) which had been dried up in vacuo before
stopping the reaction with acetic acid. The results indicate that
the only elementary reaction in this case is a hydrogen abstraction
reaction where two n-butyl groups of $n\text{-}Bu_2Zn$ were completely
consumed.

On the other hand, in a reaction with benzalacetophenone, n-butane
corresponding to 61% of n-butyl groups of $n\text{-}Bu_2Zn$ was recovered
after hydrolysis without drying up the system in vacuo. Therefore
39% of n-butyl groups must have been used in addition reactions of
$n\text{-}Bu_2Zn$ to benzalacetophenone because no sign of n-butene forma-
tion was observed, a fact which excludes the possibility of carbonyl
reduction. Thirty-seven per cent of n-butane was recovered from
the reaction mixture (reaction time, 24 hr) which had been dried up
in vacuo before stopping the reaction.

A parallel study revealed that the addition product is conjugate
adduct, I. Infrared spectra of the reaction mixture between benzal-
acetophenone and ZnR_2 are shown in Fig. 1.

$$\begin{array}{c}
C_6H_5 \\
\diagdown \\
\qquad CHCH_2COC_6H_5 \quad (\text{mp } 59.3°C) \\
\diagup \\
n\text{-}C_4H_9
\end{array}$$

I
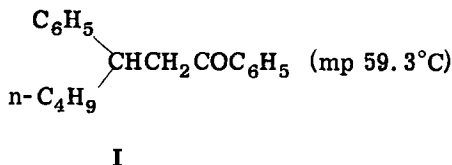
A close similarity of the IR spectrum of the reaction mixture
to that of $n\text{-}C_4H_9Zn(O\!-\!sec\!-\!C_4H_9)$ suggests that conjugate adduct
I presumably takes an enolate form such as II.

$$\begin{array}{c}
C_6H_5 \\
\diagdown \\
\qquad CH\!-\!CH\!=\!C\!-\!C_6H_5 \\
\diagup \qquad\qquad | \\
n\text{-}C_4H_9 \qquad\quad OZn\text{-}n\text{-}C_4H_9
\end{array}$$

II

The fact that 0.39 mole of n-butyl groups was consumed in the
addition reaction of 1 mole of $n\text{-}Bu_2Zn$ with benzalacetophenone
means that the formation of 0.39 mole of II took place, which should
give rise to 0.39 mole of n-butane on hydrolysis with excess acetic
acid. In accordance with this, it was confirmed by the drying-up
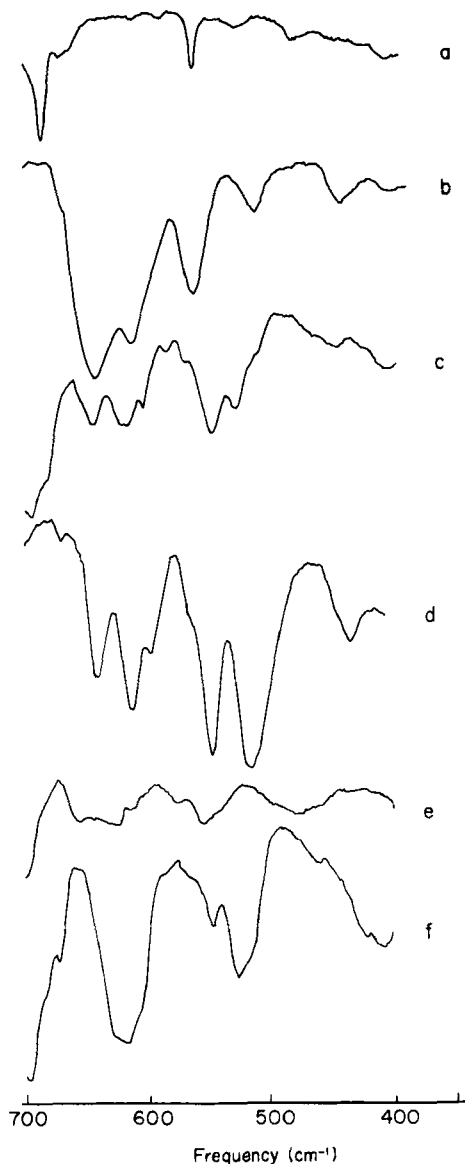
Fig. 1. Infrared spectra of organozinc compounds. (a) Saturated n-hexane solution of benzalacetophenone. (b) Benzene solution (0.64 mole/liter) of n-Bu$_2$Zn. (c) Reaction product of n-Bu$_2$Zn (0.64 mole/liter) with benzalacetophenone (1.3 mole/liter). Reaction time, 9 days at 30°C. (d) n-C$_4$H$_9$Zn-O-secC$_4$H$_9$ (0.45 mole/liter). (e) Reaction product of n-Bu$_2$Zn (0.64 mole/liter) with benzalacetophenone (1.3 mole/liter). Reaction time, 3 days at 80°C. (f) Reaction product of ZnEt$_2$ (0.50 mole/liter) with benzalacetophenone (1.0 mole/liter). Reaction time, 8 days at 30°C.

procedure that 37% of n-butyl groups of n-Bu$_2$Zn was left unchanged after a 24-hr reaction with benzalacetophenone as mentioned before. From this material balance, the reaction of n-Bu$_2$Zn with benzalacetophenone is considered to be completed after 24 hr, and the only elementary reaction besides the conjugate addition is the hydrogen abstraction reaction.

Under the conditions described in Table 2, the reactions with methyl vinyl ketone, methyl isopropenyl ketone, and methyl n-propenyl ketone yield no initial conjugate adduct, to say nothing of the n-butene or carbonyl adducts; however, 57, 52 and 85% of n-butyl groups of n-Bu$_2$Zn were recovered, respectively, as shown in Table 2.

In cases of methyl vinyl ketone and methyl isopropenyl ketone, polymerization was observed to take place under the conditions described in Table 2. Any initial adducts presumably might be consumed in the propagation step of the polymerization. To make this assumption clear the following experiments were carried out. Reaction of n-Bu$_2$Zn (0.050 mole/liter) with MVK (1.0 mole/liter) was stopped after 10 sec and methyl n-hexyl ketone (conjugate adduct) was fractionated from the reaction mixture by VPC. The infrared spectrum of the reaction product coincided almost perfectly with that of authentic methyl n-hexyl ketone, as shown in Fig. 2. Mass spectroscopy was also used for the identification.

Even in this case not a trace of carbonyl adduct was detected by VPC, but the absence of the carbonyl adduct may not necessarily mean that the carbonyl adduct had never been formed in the system, because the carbonyl adduct could be consumed completely if it has a much higher reactivity compared with the conjugate adduct

Frequency (cm⁻¹)
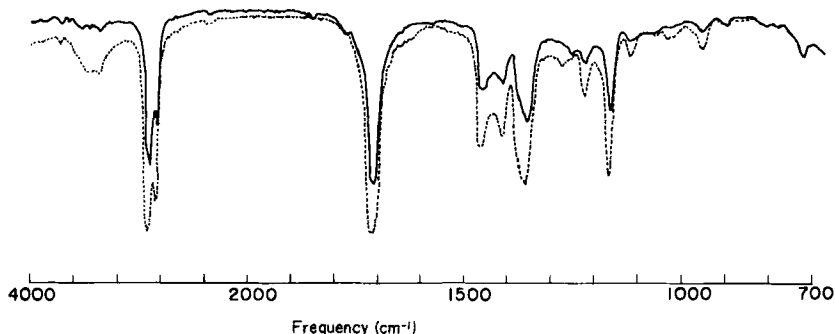
Fig. 2. Infrared spectra of the reaction products of n-Bu$_2$Zn with methyl vinyl ketone and authentic methyl n-hexyl ketone. ------, methyl n-hexyl ketone;———, reaction product (reaction time 20 sec isolated by VPC).

toward the unsaturated ketone. Therefore, the reactivities of con-
jugate and carbonyl adducts were compared. Methyl n-butyl vinyl
carbinol (MBVC) and n-Bu_2Zn give monoalkoxide of MBVC (model
compound of carbonyl adduct) quantitatively in 2 or 3 hr. Into this
reaction mixture, MVK was added. After a given time interval the
reaction products were determined by VPC. The results are shown
in Fig. 3.

   As shown in Fig. 3, the reactivity of the conjugate adduct was
found to be higher than that of carbonyl adduct. From these facts
it can reasonably be concluded that the addition reaction of n-Bu_2Zn

Fig. 3. Change in the quantities of methyl n-hexyl ketone and
methyl n-butyl vinyl carbinol in the course of reaction time, ●,
methyl n-butyl vinyl carbinol; ○, methyl n-hexyl ketone. [n-Bu_2Zn]
0.0518 mole/liter, [MBVC] 0.0168 mole/liter, [MVK] 1.20 mole/
liter.

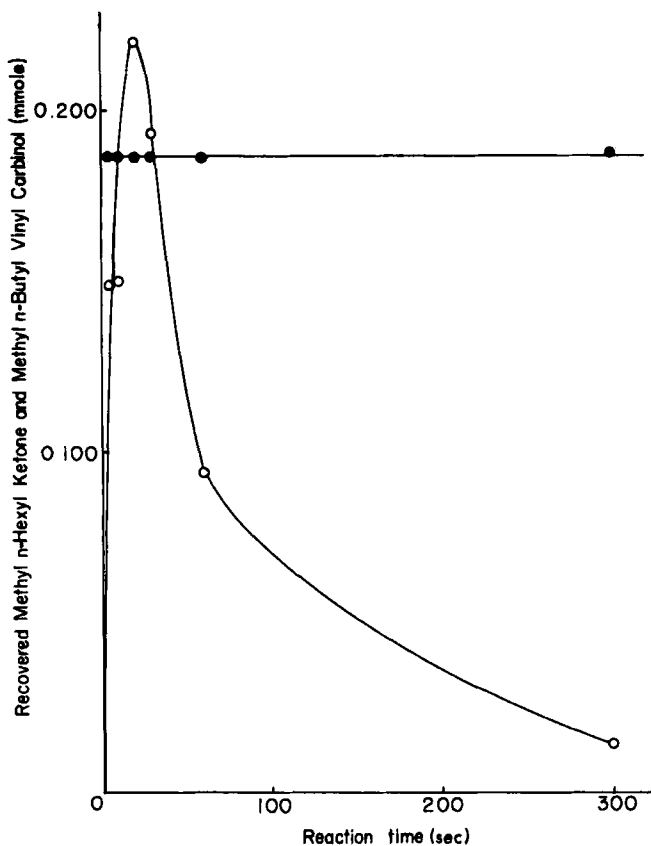to MVK takes place exclusively in the fashion of conjugate addition. MIPK and MNPK are also presumed to behave in a manner similar to MVK. Therefore, the only elementary reactions to be considered for zinc alkyl with α, β-unsaturated ketone at 30°C are hydrogen abstraction and conjugate addition reactions, though various modes of reaction, such as conjugate addition, carbonyl addition, carbonyl reduction, and hydrogen abstraction, are known to occur between other metal alkyls and α, β-unsaturated ketone, as shown in Fig. 4.

The percentage of occurrence of every elementary reaction as well as the number of alkyl groups consumed in the elementary reaction differed according to the reaction conditions, as shown in Table 1.
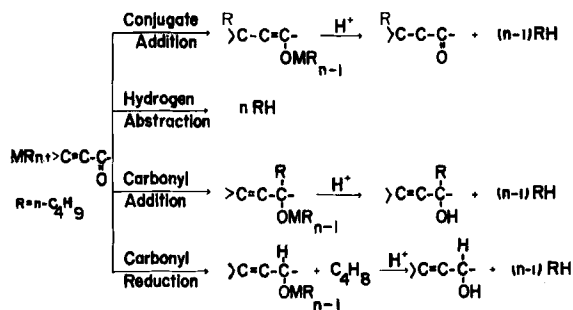
Fig. 4. Reaction modes of metal alkyls with α, β-unsaturated ketone.

Table 1. Number of Reacting Alkyl Groups Incorporated in the Reactions

Metal alkyl	Reaction		
	Conjugate addition	Hydrogen addition	Carbonyl addition
RLi[a]	1	1	1
RMgX[b]	1	1	1
AlR$_3$[a]	1	3	—
ZnR$_2$[a]	1	2	—
CaZnR$_4$[b]	2	4	—

[a]30°C in benzene. $R = n\text{-}C_4H_9$.
[b]30°C in Et$_2$O.

Table 2. Reaction of n-Bu$_2$Zn with Ketones[a]

Ketone	Reaction time, min	Recovered n-butane before drying up, %	Extent[b] conjugate addition, %	Unchanged[c] n-butyl groups after drying up, %	Conjugate addition %/ hydrogen abstraction, %
CH$_2$=CHCOCH$_3$	0	100	0	—	—
	1	83	34	—	—
	2	76	48	—	—
	3	72	56	—	—
	5	68	64	—	—
	10	63	74	—	—
	1440	57	85	41	86/14
CH$_2$=C(CH$_3$)COCH$_3$	0	100	0	—	—
	1	73	54	—	—
	2	66	68	—	—
	3	63	74	—	—
	5	59	82	—	—
	10	55	90	—	—
	1440	52	97	46	96/4
CH$_3$CH=CHCOCH$_3$	0	100	0	—	—
	1	97	6	—	—
	2	96	8	—	—
	3	95	10	—	—
	5	94	12	—	—
	10	91	18	—	—
	1440	85	30	14	30/70
C$_6$H$_5$CH=CHCOC$_6$H$_5$	0	100	0	—	—
	2	98	4	—	—
	5	93	14	—	—
	10	86	28	—	—
	1440	61	78	37	78/22
(CH$_3$)$_2$C=CHCOCH$_3$	0	100	0	—	—
	1	100	0	—	—
	5	99	1	—	—
	10	100	0	—	—
	1440	99	1	0	0/100
CH$_2$=CHCOC$_6$H$_5$	0	100	0	—	—
	1.5	58	84	—	—
	6	52	96	—	—
	60	50	100	49	100/0
C$_6$H$_5$CH=CHCOCH$_3$	1440	99	2	4	0/100
CH$_3$COCH$_3$[d]	1440	100	—	30	0/100
CH$_3$COC$_2$H$_5$[d]	1440	100	—	36	0/100
CH$_3$COC$_6$H$_5$[d]	1440	100	—	23	0/100

[a]30°C in benzene. [Ketone] 0.48 mole/liter; [n-Bu$_2$Zn] 0.025 mole/liter.

[b]Extent of conjugate addition (%) = 2 × {100(%) − recovered n-butane before drying up (%)}.

[c]Calculated from the recovered n-butane after drying up after 24 hr.

[d]It seems that unreacted n-Bu$_2$Zn remains.

On the basis of the above results, we can calculate per cent conjugate addition and per cent hydrogen abstraction by measuring recovered n-butane before and after the drying-up procedure mentioned earlier in this section. The results for the various ketones are tabulated in Table 2.

As shown in Table 2, we can assume that the n-Bu_2Zn added to MIPK and phenyl vinyl ketone almost quantitatively and in a conjugate manner, because half of the n-butyl groups of n-Bu_2Zn were recovered from the reaction mixture with the addition of acetic acid before the drying-up procedure. This n-butane can be ascribed to the second n-butyl group of n-Bu_2Zn linked with the ketone in the conjugate manner. In the reaction of n-Bu_2Zn with MVK, hydrogen abstraction, along with conjugate addition, occurred to a considerable extent. In the reaction with β-substituted compounds, such as benzalacetone and mesityloxide, all n-butyl groups of n-Bu_2Zn were consumed in hydrogen abstraction reaction. The hydrogen abstraction reaction with saturated ketones, such as acetone, methyl ethyl ketone, and acetophenone, was slower than that with α, β-unsaturated ketone. The product of hydrogen abstraction reaction with α, β-unsaturated ketone or saturated ketone could not be isolated; a complicated reaction of the initial enol-type product might be suggested.

Reaction Modes of n-Bu_3Al with α, β-Unsaturated Ketones

Between n-Bu_3Al and α, β-unsaturated ketones in benzene at 30°C, only the conjugate addition reaction and the hydrogen abstraction reaction were observed, as in the case of n-Bu_2Zn and the ketones. This was confirmed in the same way as for n-Bu_2Zn. One n-butyl group was consumed in the conjugate addition reaction and all n-butyl groups were consumed in the hydrogen abstraction reaction. The same tendency was observed in the reaction of n-Bu_3Al with α, β-unsaturated ketones, compared with that of n-Bu_2Zn with α, β-unsaturated ketones.

The results are given in Table 3.

DISCUSSION

From the above results, we attempted to calculate the rate constants of conjugate addition reactions between n-Bu_2Zn (or n-Bu_3Al) and α, β-unsaturated ketones. To calculate the rate constants, it is necessary to know the concentration of n-Bu_2Zn (or n-Bu_3Al) in the reaction system at any given time.

If the following assumptions are justified, it is possible to know total reaction rate constants and conjugate addition rate constants by measuring the recovered n-butane before the drying-up procedure at any given time.

Table 3.   Reaction of n-Bu$_3$Al with α, β-Unsaturated Ketones[a]

α, β-Unsaturated ketone	Reaction time, min	Recovered n-butane before drying up, %	Extent of conjugate addition[b], %
CH$_2$=CHCOCH$_3$	0	100	0
	1	82	54
	2	76	72
	5	71	87
	10	67	100
	1440	67	100
CH$_2$=C(CH$_3$)COCH$_3$	0	100	0
	1	78	66
	2	74	78
	5	67	98
	10	67	100
	1440	67	100
CH$_3$CH=CHCOCH$_3$	0	100	0
	2	95	15
	5	87	39
	10	83	51
	30	80	60
	1440	69	93
(CH$_3$)$_2$C=CHCOCH$_3$	0	100	0
	180	100	0
	1440	100	0
C$_6$H$_5$CH=CHCOC$_6$H$_5$	0	100	0
	1	91	27
	2	85	45
	5	76	72
	10	74	78
	30	72	84
	1440	67	100

[a]30°C in benzene, [α, β-unsaturated ketone] 0.76 mole/liter; [n-Bu$_3$Al] 0.024 mole/liter.

[b]Extent of conjugate addition (%) = 3 × {100(%) − recovered n-butane (%)}.

(i) The ratio of products of each elementary reaction (conjugate addition and hydrogen abstraction) is constant irrespective of the reaction time.

(ii) The kinetic order of each elementary reaction is the same.

We can determine the extent of conjugate addition directly by measuring the recovered n-butane before the drying-up procedure at a given time, the extent of hydrogen abstraction being calculated on the basis of product distribution at 24 hr when the reaction is found to be completed. Assumptions (i) and (ii) are found to be reasonable, as shown in Table 4.

Table 4. Influence of Concentration of $n\text{-}Bu_2Zn$ on Recovered n-Butane[a]

Ketone $\quad\quad\dfrac{[n\text{-}Bu_2Zn] \times 10^2}{\text{moles/liter}}$	2.50	1.88	1.25	0.63	0.31
$CH_2{=}CHCOCH_3$	57	56	57	55	58
$CH_2{=}C(CH_3)COCH_3$	52	53	52	51	—

[a]Percentage of recovered n-butane before drying up, after 24 hr; [ketone] 0.50 mole/liter.

According to Table 4, the percentage of recovered n-butane before drying up after 24 hr is almost constant regardless of the concentration of $n\text{-}Bu_2Zn$. This not only means that the percentage of the two elementary reactions is constant irrespective of the reaction time, but also that the kinetic orders of the reactions are the same.

Therefore, the total rate constant, k, can be written as

$$k = k_c + k_h \tag{1}$$

where k_c is a conjugate addition rate constant and k_h is a hydrogen abstraction rate constant, k_c is calculated from Eq. (2):

$$k_c = k \times \text{(the fraction of conjugate addition)} \tag{2}$$

The conversions of $n\text{-}Bu_2Zn$ and $n\text{-}Bu_3Al$ were calculated from the data in Tables 2 and 3 and are listed in Tables 5 and 6, respectively.

The data in Tables 5 and 6 were found not to correspond with the first-order rate law. When a second-order reaction with respect to the metal alkyl was assumed, excellent linear relationship

Table 5. Conversion of n-Bu_2Zn with α, β-Unsaturated Ketones

α, β-Unsaturated ketone	Reaction time, min	Conversion of n-Bu_2Zn,%
$CH_2=CHCOCH_3$	0	0
	1	40
	2	57
	3	66
	5	76
	10	87
	1440	100
$CH_2=C(CH_3)COCH_3$	0	0
	1	56
	2	70
	3	77
	5	85
	10	94
	1440	100
$CH_3CH=CHCOCH_3$	0	0
	1	20
	2	27
	3	33
	5	44
	10	72
	1440	100

was obtained between $\{X_0/X - 1\}$ and time t, where X is the concentration of metal alkyl at time t, and X_0 is the concentration of metal alkyl at time 0.

Then the rate equation can be written:

$$\{X_0/X - 1\} = kX_0M^nt \tag{3}$$

where m is the concentration of ketone. As M was used in excess relative to X_0, M might be assumed to be constant throughout the reaction. To confirm the validity of Eq.(3), further experiments were carried out in which the concentration of metal alkyl was half that of metal alkyl in Tables 5 and 6. The results are shown in Figs. 5 and 6.

The straight lines in Figs. 5 and 6 show that the reaction between metal alkyl and α, β-unsaturated ketone is a second-order reaction with respect to the metal alkyl. Dependence of reaction rate on the concentration of ketone M was also checked.

Table 6. Conversion of n-Bu₃Al with α, β-Unsaturated Ketones

α, β-Unsaturated ketone	Reaction time, min	Conversion of n-Bu₃Al, %
CH₂=CHCOCH₃	0	0
	1	54
	2	72
	5	87
	10	100
	1440	100
CH₂=C(CH₃)COCH₃	0	0
	1	66
	2	78
	5	98
	10	100
	1440	100
CH₃CH=CHCOCH₃	0	0
	2	16
	5	42
	10	55
	30	65
	1440	100
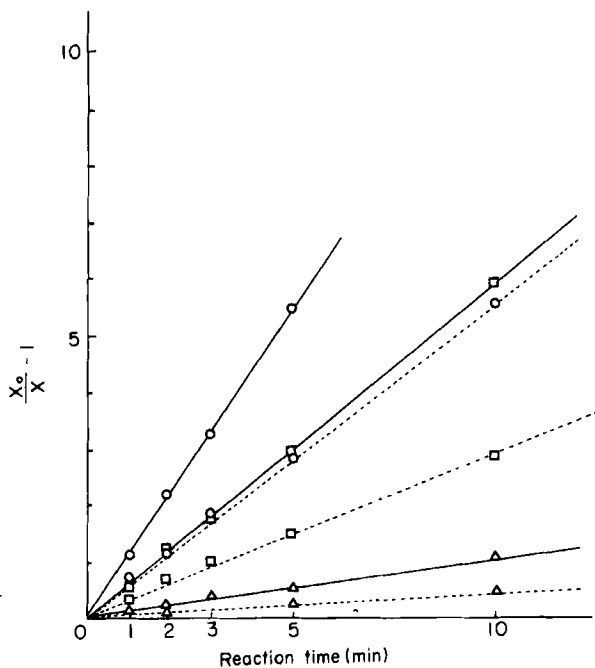
Fig. 5. Reaction of n-Bu₂Zn with α, β-unsaturated ketones. ○, methyl isopropenyl ketone; □, methyl vinyl ketone; △, methyl n-propenyl ketone. 30°C in benzene. [Ketone] 0.48 mole/liter. ———, [n-Bu₂Zn] 0.025 mole/liter; ------, [n-Bu₂Zn] 0.0125 mole/liter.
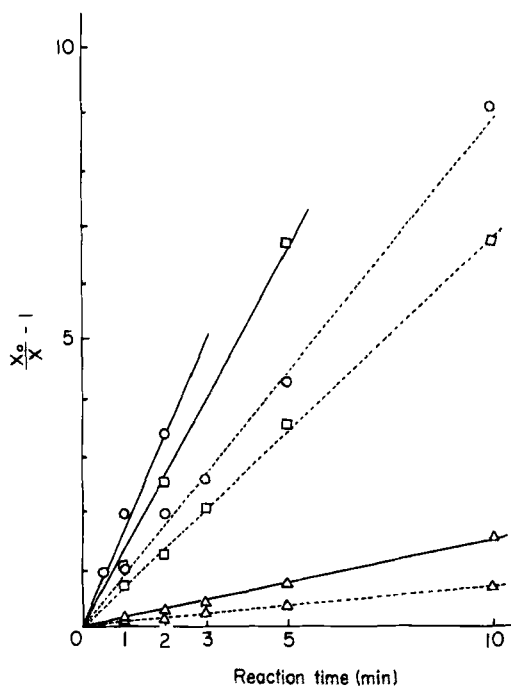
Fig. 6. Reaction of n-Bu$_3$Al with α,β-unsaturated ketones. $\bigcirc$, methyl isopropenyl ketone; $\square$, methyl vinyl ketone; $\triangle$, methyl n-propenyl ketone. 30°C in benzene. [Ketone] 0.76 mole/liter.

Figure 7 shows that the initial rate of the reaction between metal alkyl and α,β-unsaturated ketone is expressed as a first-order reaction with respect to α,β-unsaturated ketone. From Figs. 5 and 6, k and k$_c$ were calculated.

As shown in Tables 1 and 7, the reactivity in conjugate addition is decreased in the following order: phenyl vinyl ketone > methyl isopropenyl ketone > methyl vinyl ketone > methyl n-propenyl ketone. The reactivity of the α-methyl-substituted ketone is larger than the unsubstituted one, while the reactivity of the β-methyl-substituted ketone is extremely small. This order of reactivity is similar to the order of radical affinity of vinyl compounds [4]. In an earlier paper [4], Tsuruta and Yasuda reported the linear relationship between log k$_H$/k$_\alpha$ and log k$_\beta$/k$_\alpha$, where k is the rate constant of the relevant conjugate addition reaction, subscripts H, α, and β are concerned with the unsubstituted, α-methyl-substituted, and β-methyl-substituted compounds. Points located at the upper

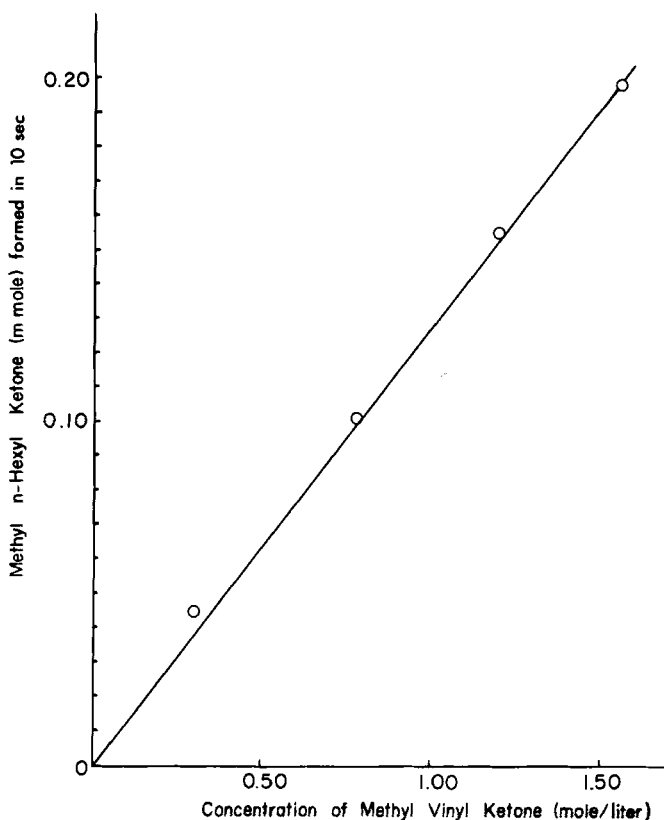**Fig. 7.** Dependence of reaction rate on the concentration of ketone. [n-Bu$_2$Zn] 0.0388 mole/liter, at 30°C. Reaction time, 10 sec.

**Table 7.** Total Rate Constants and Conjugate Addition Rate Constants[a]

Constant	Metal alkyl	CH$_2$=CHCOCH$_3$	CH$_2$=C(CH$_3$)COCH$_3$	CH$_3$CH=CHCOCH$_3$
k	n-Bu$_2$Zn	52	96	19
	n-Bu$_3$Al	66	99	6.9
k$_c$	n-Bu$_2$Zn	44	95	5.7
	n-Bu$_3$Al	66	99	6.5

[a]Rate constant (liter^2/mole^2 min).

right portion of the line represent reactions having strong hetero-lytic character, in contrast with points at the lower left. Plots for the reactions of α, β-unsaturated ketone with n-Bu_2Zn or n-Bu_3Al were found to fall at the extreme left and bottom, a fact which suggests the homolytic character of these reactions.

In the light of the results above, the four-centered mechanism seems to be plausible for the conjugate addition reaction of n-Bu_2Zn or n-Bu_3Al to α, β-unsaturated ketones:

$$R: n\text{-}C_4H_9$$
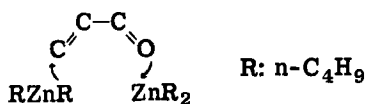
This four-centered mechanism might have some relation to the fact that methyl vinyl ketone was polymerized to stereoregular polymer by ZnR_2 or AlR_3 catalyst.

In order to determine solvent effects, some experiments in tetrahydrofuran were also carried out. The results are shown in Table 8.

Table 8. Conjugate Addition Reaction Rate Constants in THF[a]

Metal alkyl \ Ketone	$CH_2=CHCOCH_3$	$CH_2=C(CH_3)COCH_3$	$CH_3CH=CHCOCH_3$
n-Bu_2Zn	370	320	32
n-Bu_3Al	2200	1700	260

[a]Rate constant (liter^2/mole^2 min).

The reactivities of methyl vinyl ketone and methyl isopropenyl ketone in tetrahydrofuran are transposed. And the plots of $\log k_H/k_\alpha$ vs. $\log k_\beta/k_\alpha$ are found to shift considerably to the heterolytic part of the straight line.

ACKNOWLEDGMENT

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