Aluminum Chloride Catalyzed Diene Condensation. IV.[1] Kinetic Study of Butadiene–Methyl Acrylate Reaction

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The rate of the aluminum chloride catalyzed diene condensation between butadiene and methyl acrylate in benzene solution is expressed by rate = k_c[butadiene][methyl acrylate–aluminum chloride complex]. E_a and log A (l./mole sec) were found to be 10.4 ± 1.9 kcal/mole and 4.8 ± 1.4, respectively. E_a and log A for the corresponding uncatalyzed reaction were found to be 18.0 ± 1.0 kcal/mole and 5.4 ± 0.6, respectively. Some mechanistic implications of these results are discussed.

The nature of catalytic actions of aluminum chloride on the diene condensation of α,β-unsaturated carboxylic esters has been studied by determining the substituent effects on the rate and orientation[1,2] and the stereochemical selectivity of the reaction.[1,3,4] The results of studies of substituent effects indicated the importance of the heterolytic nature of the reaction and it was suggested, with some reservation, that the reaction involves two electronic reorganization steps, one corresponding to the electrophilic attack of the β carbon of the dienophile on a terminus of the 1,3-diene and the other corresponding to the ring-closure step.[2] The remarkably higher *endo* selectivity of the catalyzed reaction, however, showed its stronger adherence to the steric course of the parallel biplanar approach of addends with maximum accumulation of centers of unsaturation, well known for the uncatalyzed reaction,[5] in favor of one-step reaction mechanism.[3] Most of Diels–Alder reactions have abnormally low pre-exponential factor ($\sim 10^{4-7.5}$ l./mole sec) for bimolecular reaction, and this fact is in conformity with the highly restricted mutual orientation of the addends in the transition state.[6] It is therefore of interest to know whether the pre-exponential factor of the catalyzed reaction is likewise small or not. In this article the kinetic expression of the catalyzed reaction was investigated and the Arrhenius parameters of the condensation between butadiene and methyl acrylate in benzene in the presence and absence of aluminum chloride were determined.

Results and Discussion

The uncatalyzed reaction is much slower than the catalyzed one, as will be shown below; hence its contribution to the total rate is negligible in the kinetic studies of the catalyzed reaction. The amount of aluminum chloride was kept below the equivalent of methyl acrylate in all the kinetic runs because the excessive aluminum chloride will catalyze undesirable side reactions such as the cationic polymerization and Friedel–Crafts reaction with solvent benzene.

A typical kinetic run with the initial concentrations of 9.65×10^{-2} mole/l. of butadiene and 18.4×10^{-2} mole/l. of methyl acrylate in benzene in the presence of 0.663×10^{-2} mole/l. of aluminum chloride is shown

in Figure 1, in which the rate of formation of the adduct is assumed to be first order in butadiene alone. The treatment of the data with the second-order assumption, first order in both the reactants, was found unsuitable. This will be explained by assuming that the active reagent is methyl acrylate–aluminum chloride complex (MA–AlCl$_3$) whose concentration is determined by the analytical concentration of aluminum chloride and, hence, is essentially constant as long as enough methyl acrylate remains in the system to regenerate MA–AlCl$_3$ efficiently. Thus, the concentration of methyl acrylate in excess of that of aluminum chloride will not affect the rate of reaction at the early stage of the kinetic run. As the reaction proceeds to a greater extent and an increasing amount of the product begins to compete with methyl acrylate for aluminum chloride, the rate gradually falls off the first-order line.

Effect of concentration of aluminum chloride on the pseudo-first-order rate is shown in Figure 2. This shows that the rate is proportional to the concentration of aluminum chloride, hence of MA–AlCl$_3$, although extrapolation to zero rate slightly deviates from the origin (1.12 mmole/l. of aluminum chloride by least-squares treatment). This small intercept is probably due to deterioration of part of aluminum chloride used by moisture present in the system. The second-order rate constant, k_c, shown in Table I, has been calculated based on the concentration of aluminum chloride corrected for this loss.

TABLE I
EFFECT OF CONCENTRATION OF ALUMINUM CHLORIDE ON THE RATE[a]

AlCl$_3$,[b] mmoles/l.	AlCl$_3$,[c] mmoles/l.	t^{-1} (sec) × 2.303 log $(a/a - x)$	k_c, l./mole sec[d]
3.23	2.11	2.69 × 10^{-6}	1.27 × 10^{-3}
6.31	5.19	6.49 × 10^{-6}	1.25 × 10^{-3}
9.22	8.10	9.83 × 10^{-6}	1.21 × 10^{-3}
12.99	11.87	14.7 × 10^{-6}	1.24 × 10^{-3}

[a] Reaction at 20°; initial concentration of butadiene, a, 20.94 mmoles/l.; that of methyl acrylate, 44.4–44.6 mmoles/l. [b] Uncorrected. [c] Corrected. See text for the correction of concentration of aluminum chloride. [d] t^{-1} (sec) × 2.303 log $(a/a - x)$ divided by aluminum chloride corrected; cf. eq 3.

The concentration of methyl acrylate has been found to have essentially no effect on the rate constant over a wide range as is seen from Table II. Thus, at the concentration of aluminum chloride of 5 mmole/l., it can be increased from 1.7 to 42 times that of aluminum chloride without meaningful change of the rate constant. This clearly shows that MA–AlCl$_3$ is the true reagent and the uncomplexed methyl acrylate does not come

(1) Paper III: Inukai, T., and Kojima, T., *J. Org. Chem.*, **32**, 869 (1967).
(2) T. Inukai and T. Kojima, *ibid.*, **31**, 1121 (1966).
(3) T. Inukai and T. Kojima, *ibid.*, **31**, 2032 (1966).
(4) J. Sauer and J. Kredel, *Tetrahedron Letters*, 731 (1966).
(5) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961), section V.
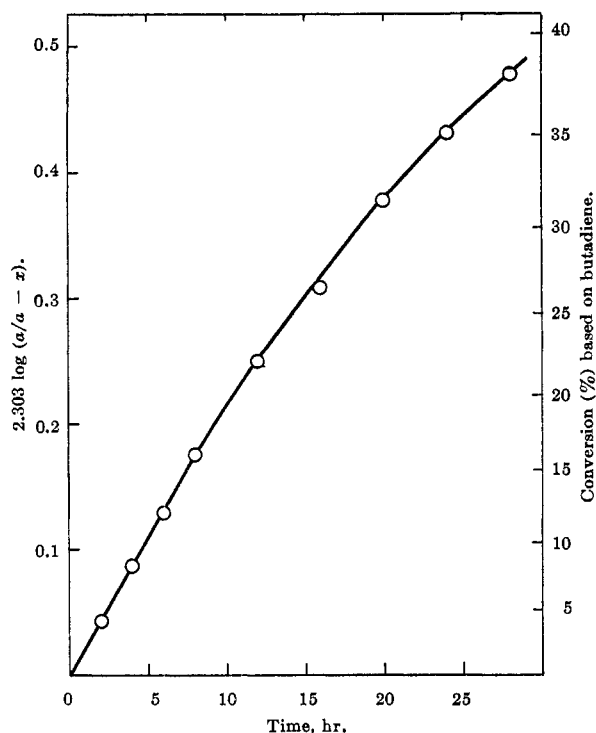(6) A. Wassermann, "Diels–Alder Reactions," Elsevier Publishing Co., Amsterdam, 1965, Chapter 4.

Figure 1.—First-order plot of rate of reaction at 20°: initial concentration of butadiene, a, 9.65 × 10^{-2} mole/l.; that of methyl acrylate, 18.4 × 10^{-2} mole/l.; that of aluminum chloride, 0.663 × 10^{-2} mole/l.; solvent, benzene.
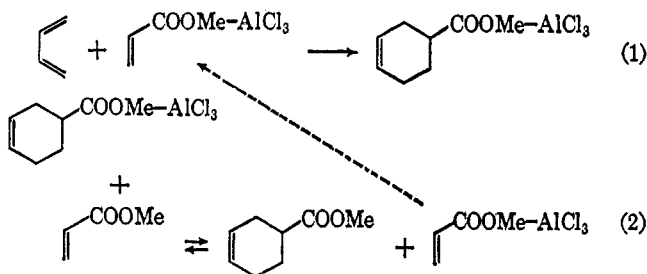
in the kinetic expression of the catalyzed reaction. Since polymerization and Friedel–Crafts reactions of butadiene do not occur and benzene-insoluble aluminum chloride is dissolved in the solution under the present experimental conditions, all of the aluminum chloride used must be assumed to be in a form of soluble complex.

TABLE II

EFFECT OF CONCENTRATION OF
METHYL ACRYLATE ON THE RATE CONSTANTS[a]

Methyl acrylate, mmoles/l.	$AlCl_3$, mmoles/l.[b]	k_c, l./mole sec
8.632	4.94	1.13 × 10^{-3}
44.55	5.19	1.25 × 10^{-3}
111.9	5.40	1.15 × 10^{-3}
224.2	5.29	1.07 × 10^{-3}

[a] Reaction at 20°; initial concentration of butadiene, 20.94 mmoles/l.   [b] Corrected.

It is concluded therefore that the reaction scheme is presented by eq 1 and 2.   Equation 1 represents the

$$\text{(diene)} + \overset{\text{COOMe–AlCl}_3}{||} \longrightarrow \overset{\text{COOMe–AlCl}_3}{\bigcirc} \qquad (1)$$

$$\overset{\text{COOMe–AlCl}_3}{\bigcirc} + \overset{\text{COOMe}}{||} \rightleftharpoons \overset{\text{COOMe}}{\bigcirc} + \overset{\text{COOMe–AlCl}_3}{||} \qquad (2)$$

rate-determining step and eq 2 serves to regenerate the MA–$AlCl_3$ fast enough to keep its concentration ma-
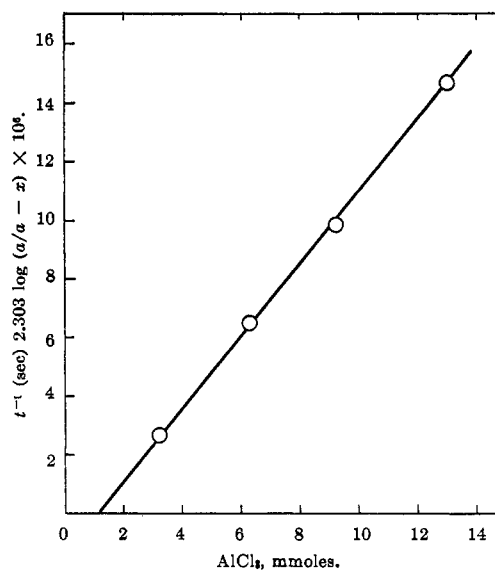

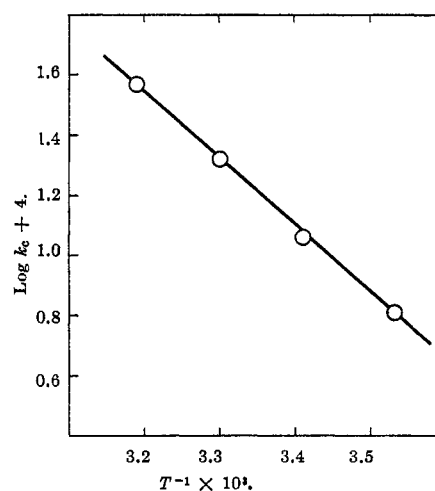Figure 2.—Effect of concentration of aluminum chloride on pseudo-first-order rate constant at 20° (cf. Table I).

Figure 3.—Arrhenius plot of rate constant, k_c, of the catalyzed reaction: from top to bottom, at 40, 30, 20, and 10°.

terially constant.   The kinetic expression is given by eq 3.

$$\text{rate} = k_c[\text{butadiene}][\text{MA–AlCl}_3] \qquad (3)$$

Activation Parameters.—The temperature dependence of k_c is summarized in Table III and its Arrhenius plot is shown in Figure 3.   The activation energy and log A (l./mole sec) factor are calculated to be 10.4 ± 1.9 kcal/mole and 4.8 ± 1.4,[7] respectively (ΔS^*, −37.7 eu).

TABLE III

TEMPERATURE DEPENDENCE OF RATE CONSTANT k_c[a]

Temp, °C	k_c, l./mole sec
10	0.64 × 10^{-3}
20	1.15 × 10^{-3}
30	2.08 × 10^{-3}
40	3.68 × 10^{-3}

[a] Initial concentration of butadiene, 5–35 mmoles/l.; that of methyl acrylate, 44.74 mmoles/l.; that of aluminum chloride (corrected), 5.10 mmoles/l.

(7) 95% confidence limit.

The second-order rate constant for the uncatalyzed reaction of butadiene and methyl acrylate in benzene is summarized in Table IV. The activation energy and log A (l./mole sec) factor are calculated to be 18.0 ± 1.0 kcal/mole and 5.4 ± 0.6,[7] respectively (ΔS^*, -36.2 eu).

TABLE IV

TEMPERATURE DEPENDENCE OF RATE CONSTANT k_u OF UNCATALYZED REACTION[a]

Temp, °C	k_u, l./mole sec
60	0.408×10^{-6}
70	0.885×10^{-6}
80	1.92×10^{-6}
90	3.80×10^{-6}

[a] Reaction in benzene. Initial concentration of butadiene, 0.424 moles/l.; that of methyl acrylate, 6.407 moles/l.

The rate constant, k_u, at 20° is calculated to be 1.00×10^{-8} l./mole sec by extrapolation. The enhancement of rate constant by aluminum chloride at 20° is by a factor of as large as 10^5, and this big acceleration is entirely due to the lowering of the activation energy.

The pre-exponential factor of the catalyzed reaction is approximately equal to that of the corresponding uncatalyzed reaction and is quite normal for the Diels–Alder reactions. Consequently, the catalyzed reaction also proceeds with the equally restricted spatial arrangement of the addends, i.e., butadiene and MA–AlCl$_3$, in the transition state of the rate-determining step.

Kinetic studies of catalysis of the cyclopentadiene–benzoquinone reaction by Brønsted acids have shown that the rate is expressed by eq 4, where a and $a - x$

$$dx/dt = k_u(a - x)^2 + k_c z(a - x)^2 \qquad (4)$$

are the equimolecular concentrations of diene and dienophile at zero time and time t, z is the catalyst concentration, k_u is the second-order rate constant of the uncatalyzed reaction, and k_c is the catalytic rate constant.[6] The equilibrium of association between the dienophile and acids has to be taken into account to interpret this kinetic expression. It is of interest to note that log A_c (l.^{2}/mole^2 sec) is smaller than log A_u (l./mole sec) by an average of ca. 3. This difference is comparable with that expected between termolecular and bimolecular reactions from the collision theory. It is supposed, therefore, that both log A_c and log A_u are depressed from the normal values for the reactions of the corresponding molecularities by approximately the same amount because of comparable decreases of freedom by formation of the restricted transition complexes.

Our finding of the same log A value for the catalyzed and uncatalyzed reactions is thought to agree with that of Wassermann, et al.,[6,8] in that both reactions suffer from loss of freedom of the same amount in the transition states; the kinetic expression of our system is simpler because firstly a tight complex is formed between MA and AlCl$_3$ and secondly k_c is much larger than k_u.

The catalyzed reaction may be interpreted to proceed in the following pathways. The β carbon of MA is made more positive by complex formation. The electrophilic β carbon of MA–AlCl$_3$ will approach one terminus (1) of the 1,3-diene system along the axis of the bond (1–1') about to be formed, perpendicular to the plane of the cisoid conformation of the diene. As the two electrons (at 1 and 2) are progressively involved in the new bond to a fuller extent, the other electrons (at 3 and 4) will delocalize over the 2 position and electronic and electrodynamic interactions involving 2' position will stabilize the biplanar arrangement compared with other thinkable conformations. At the same time the electron-deficient system, (2–3–4)$^+$, will interact with the complexed carboxylate group with associated energy of ca. 0.3 kcal/mole,[9] to fix the conformation of the carboxylate group around 1–1' bond to that shown in the figure, and will also interact with the substituent R if it is available (I). The substituent effect and endo selectivity will be more pronounced in I than in the less polar transition state II of the uncatalyzed reaction as conceived according to the "two-stage" mechanism (Scheme I) of Woodward and Katz.[10]

SCHEME I
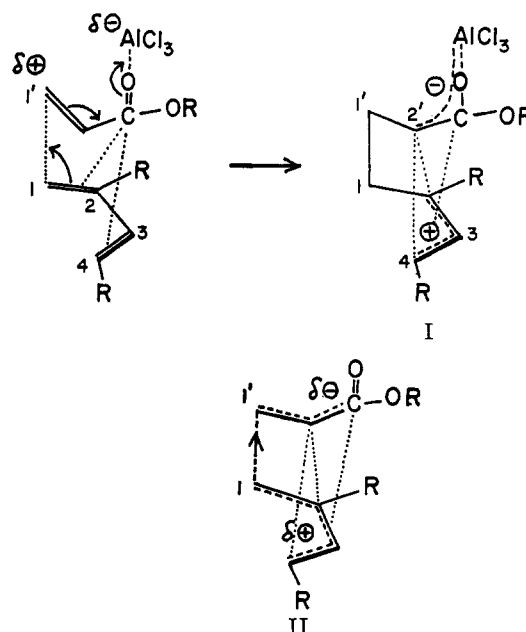
The difference of the mechanism may be indicated also by the following considerations. The fact that MA–AlCl$_3$ is more dienophilic than free methyl acrylate is beyond doubt since the former reacts with lower activation energy; yet it is more sensitive to the substituent effect.[1,2] This is in a sharp contrast to the theoretical expectation that a more reactive reagent will be less selective generally.[11] However, it would be noted that this expectation may be reliable only when the reactions to be compared are of such similar electronic characteristics that their rates can be theoretically correlated with each other in terms of dif-

(8) W. Rubin, H. Steiner, and W. Wassermann, J. Chem. Soc., 3046 (1949).

(9) Calculated from the endo or cis selectivity of 95% assuming that the π interactions are the sole reason for the selectivity.

(10) R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959).

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 6.

ferentials of appropriate reaction parameters. It is suggested, therefore, that these two reactions under the present investigation will differ from each other rather drastically in nature, presumably in the mechanism in which electrons are supplied from the diene to the dienophile moiety in the transition state. Thus, the catalyzed reaction is assumed to start with electrophilic attack of β carbon of MA–AlCl$_3$ on the diene to give I, if the uncatalyzed reaction is to proceed through the four-center-type[10,12] pathways. There will be no reason to believe that the exchange interaction between 4 and 2' positions begins *after* the initial bond (1–1') is completed. The question of whether the two new bonds are formed simultaneously or sequentially is therefore a subtle problem of whether the potential-energy profile is one peaked or two peaked.

Although the heterolytic mechanism is probable as discussed here, the possibility of four-centered mechanism for the catalyzed reaction can not be definitely ruled out because the larger selectivity might possibly be explained by assuming a larger polarity of 1–1' bond induced by the inductive effect of the complexed carboxylate group. It is possible that the reactivity-selectivity correlation may fail when the reactivities of reagents differ very extremely, even if the reactions belong to the same broad category of the reaction mechanisms.

(12) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 453.

Experimental Section

Aluminum Chloride Catalyzed Reaction.—A 300-ml, three-necked round-bottomed flask, fitted with a mercury-sealed stirrer, an inlet for nitrogen, and another inlet guarded with a mantle for stream of dry nitrogen, was placed in a thermostat. A benzene solution (50 ml) of MA–AlCl$_3$ of a known concentration containing known amounts of tetraline and methyl acrylate was added to the above reaction flask which had been flushed with dry nitrogen. A dilute benzene solution (100 ml) of butadiene of a known concentration, which had been thermally equilibrated in the same bath, was rapidly added to the flask. After certain time intervals aliquats were taken out onto 25 ml of water to stop the reaction. The benzene layer was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The concentrate was analyzed for the amount of the product formed by glpc.

Uncatalyzed Reaction.—A benzene solution containing methyl acrylate (6.407 moles/l.), butadiene (0.424 mole/l.), and tetraline (0.09513 mole/l.) was prepared by using a high vacuum line. Portions of this solution were transfered to small tubes (4 mm i.d. × 50 mm) in a closed system and were sealed off. After certain periods of reactions in a thermostat the tubes were opened and the contents were directly analyzed for the addend by glpc.

Registry No.—Butadiene, 106-99-0; acrylic acid methyl ester, 96-33-3.

9-Decalyl Free Radicals.   Decomposition of *cis*- and *trans*-9-Decalylcarbinyl Hypochlorite[1a]

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9-Decalyl radicals have been examined by the free-radical chain decomposition of *cis*- and *trans*-9-decalylcarbinyl hypochlorite in fluorotrichloromethane. Chain lengths exceed 1000 for the decomposition of both hypochlorites. The major products are formaldehyde and *cis*- and *trans*-9-chlorodecalin. The product ratio, *trans*-RCl/*cis*-RCl, obtained from *trans*-hypochlorite is independent of initial hypochlorite concentration and favors the *trans*-chloride (30 to 1 at −40°, 15 to 1 at 0°). The product ratio from *cis*-hypochlorite is dependent on the initial concentration of hypochlorite and favors the *cis*-chloride at high concentration and low temperature (1.3 to 1 at 3 M, −80°); at low hypochlorite concentrations the product ratio is the same as that obtained at all concentrations from *trans*-hypochlorite. The results require two different 9-decalyl radicals: one from *cis*-hypochlorite that either isomerizes to the radical derived from *trans*-hypochlorite or abstracts chlorine from hypochlorite to give *cis*- (and possibly some *trans*-) 9-chlorodecalin; and one from *trans*-hypochlorite that reacts with hypochlorite to give both 9-chlorodecalins, mainly the *trans* isomer, but does not isomerize to the radical initially formed from the *cis*-hypochlorite. The relevance of these results to questions of conformation and radical geometry is discussed.

Stereochemistry of atom-transfer reactions to carbon radicals has been a subject of interest to us. A relevant question is the geometry of carbon radicals. Spectroscopic evidence indicates planarity for the methyl radical.[2] Much data from electron spin resonance spectroscopy have been interpreted in terms of planar carbon radicals.[3] A study of relative rates of chlorine

abstraction from carbon tetrachloride *vs.* decarbonylation of acyl radicals has led to the conclusion that the bridgehead radicals, 1-[2.2.2]bicyclooctyl and 1-adamantyl, are more stable than *t*-butyl.[4] An esr study of fluorinated methyl radicals has provided a strong indication that these are nonplanar (CF$_3$· almost tetrahedral, with a gradual change toward planarity as fluorine is replaced by hydrogen).[5] Since a group such as methyl may be regarded as isoelectronic with fluorine atom, the study provides new impetus to the search

(2) G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).
(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).
(4) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).
(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).