

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Some Gaseous Diels-Alder Reactions

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All association reactions of the type $M_2 + M_3 \rightarrow M_1$ can be conveniently divided into two classes: (1) atomic associations and (2) molecular associations. Whereas the association of atoms is usually the result of a triple collision, there exists experimental evidence showing that molecular associations can result from a double collision. Reactions which bear this out are the hydrogenation of ethylene,¹ polymerization of ethylene,² butadiene,³ and isoprene.⁴

The Diels-Alder Reaction.⁵—Compounds containing a system of conjugated double bonds are capable of adding in the 1,4-position molecules which contain either an active ethylenic or acetylenic bond and thus forming a partially hydrated six-membered ring. A great variety of conjugated and active ethylenic compounds will undergo this reaction, yielding a large number of different types of products. It may be pointed out that if the reaction leads to the formation of a bridged ring, then this product is unstable and can be decomposed by heating. In some cases the reaction can be reversed even at room temperature merely by making a dilute solution of the product.⁶ Furthermore, compounds containing the group $C=C-C\equiv C$ are capable of functioning either as conjugated reaction partners or as active ethylenic compounds. Accordingly, they can react with themselves. As examples may be mentioned the polymerization of 1,3-butadiene, isoprene and cyclopentadiene.

Reaction rate measurements in the gaseous phase were carried out with the four reactions. Diels and Alder⁷ have studied these reactions and have established the structure of the aldehydes formed. Their work was all done in solution and no kinetic measurements were undertaken.

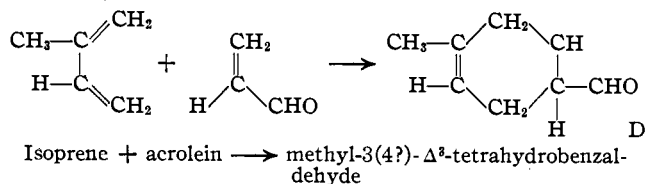
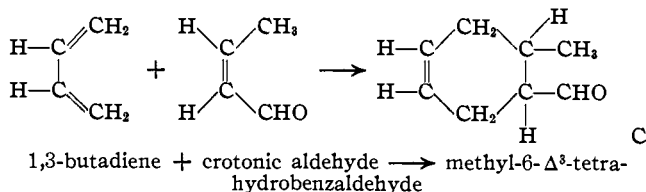
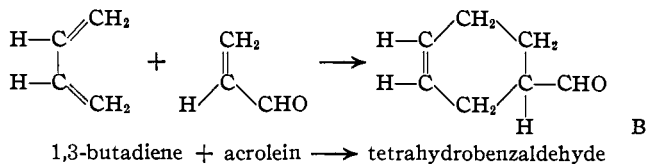
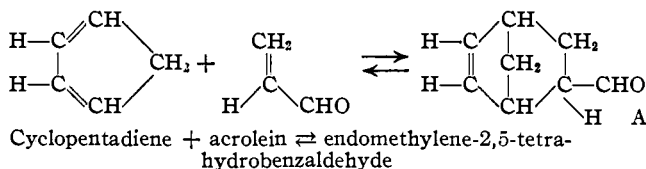
(1) Pease, *THIS JOURNAL*, **54**, 1876 (1932).(2) Pease, *ibid.*, **53**, 613 (1931).(3) Vaughan, *ibid.*, **54**, 3863 (1932).(4) Vaughan, *ibid.*, **55**, 4109 (1933).

(5) "Handbuch der biologischen Arbeitsmethoden: Die Methoden der Dien-synthesen," Kurt Alder, 1933.

(6) Kohler and Kable, *THIS JOURNAL*, **57**, 917 (1935).(7) Diels and Alder, *Ann.*, **460**, 119 (1928); *ibid.*, **470**, 68 (1929).

Description of Apparatus

The reaction vessel (1000-cc. Pyrex flask) was connected to two metal needle valves (with sylphon bellows instead of packing) and to a quartz spiral manometer by means of 2-mm. capillary tubing. The metal valves communicated to purification traps and to a mercury vapor pump. A mercury manometer was used in conjunction with the quartz spiral. The reaction vessel was placed in an electric furnace consisting of a well insulated large copper block. There were no temperature gradients in the furnace (to $\pm 0.2^\circ$); the temperature was regulated manually to a constancy of $\pm 0.1^\circ$ even during long runs. A chromel-copel thermojunction served to measure the absolute temperature and was calibrated against a platinum resist-



ance thermometer. All parts of the reaction system outside of the furnace were electrically heated.

Purification of Materials

Acrolein.—This was a product of the Eastman Kodak Co., No. 2037. It was stated to have been prepared by dehydrating glycerol and contained 0.1% hydroquinone as a stabilizer; b. p. $51-55^\circ$.

To purify the material further, it was cooled to -78° whereupon white flaky crystals separated out. They were filtered off by forcing the liquid through a tube containing glass wool. After two filtrations, the liquid would remain perfectly clear at this temperature. Ordinarily this puri-

fied acrolein would be stored in a trap at room temperature with a little hydroquinone. This trap was painted black. One sample of acrolein was filtered once at -80° and then fractionated in a vacuum-jacketed still. It had a boiling range of $52.85-53.05^{\circ}$.

Crotonic Aldehyde.—This was also an Eastman product, No. 1878; b. p. $102-103^{\circ}$. The material was stored as such in the absence of light and air and in the presence of hydroquinone.

Endomethylenetetrahydrobenzaldehyde.—This was made according to the method of Diels and Alder.⁷ An excess of acrolein was used to minimize the polymerization of the cyclopentadiene. The material was then distilled directly into a storage trap. The product was a colorless liquid and was stored at room temperature in the absence of light.

Isoprene.—This was an Eastman product, No. 2542. It was separated from the polymer it contained by distilling at low pressures directly into the storage trap. This trap contained a little hydroquinone and was painted black. The isoprene was stored at room temperature.

Butadiene.⁸—The butadiene used in these experiments was prepared in two ways. Sample H was obtained by cracking cyclohexene and was purified by distillation. It had a boiling range of 0.02° . This sample was used in runs 1 to 6 with acrolein, and in all runs made with crotonic aldehyde and the polymerization experiments. Sample D was prepared by reducing tetrabromobutane and had a boiling range of 0.01° . This was used in runs 7 to 15 with acrolein. Both samples were stored at dry-ice temperature.

Cyclopentadiene.—This material was obtained by cracking technical dicyclopentadiene. A thermometer in the top of the cracking column registered $40-41^{\circ}$ during the entire depolymerization. The monomer obtained was subjected to a fast distillation. The boiling range of the fraction saved was $40.1-40.3^{\circ}$. This monomer was then polymerized by heating on a steam-bath. The dimer obtained was distilled twice under reduced pressure, after which it was a colorless solid, freezing at 33.6° .

The cyclopentadiene used in these experiments was obtained by cracking the purified dimer. The material was stored at dry-ice temperature in the presence of a little hydroquinone.

Experimental Details and Calculations

Acrolein and Cyclopentadiene.—A preliminary experiment in which a mixture of cyclopentadiene and acrolein was slowly heated from 100 to 300° showed first a decrease and then an increase in pressure, indicating that a reversible reaction was taking place.

In order to make a run a small sample of acrolein from the storage trap was subjected to two bulb-to-bulb distillations. Only the middle fraction was saved in each case. Since the sample of cyclopentadiene was fairly pure, bulb-to-bulb distillations were used mainly to remove dissolved air. The acrolein was then distilled into the reaction vessel by warming the trap with a water-bath. In practically all of the runs, acrolein was admitted first because preliminary experiments showed that it was stable

up to temperatures of about 330° . At this temperature, however, it undergoes slow decomposition.

After the initial pressure of acrolein had been read, the cyclopentadiene was distilled into the reaction vessel in the same manner. The initial time of the reaction was counted the instant one-half of the total amount of the cyclopentadiene had been admitted, and the total initial pressure was obtained by graphical extrapolation. Once this total pressure was known, the initial pressure of the cyclopentadiene was obtained by subtracting from it the initial pressure of the acrolein. The rate of the reaction was then followed by taking pressure readings at various times. When the reaction was complete, or had been followed for as long a time as was convenient, the 0.1° mercury thermometer was removed from the reaction vessel and the absolute temperature taken with a thermocouple.

The nature of the product of the reaction was established by condensing it out and distilling off the unreacted acrolein and cyclopentadiene. The heavy oil remaining was collected, dissolved in alcohol, and treated with a freshly prepared aqueous solution of sodium carbonate and semicarbazide hydrochloride. The white precipitate formed was recrystallized out of aqueous methyl alcohol three times and had a melting point of $159-162^{\circ}$. A small amount of endomethylenetetrahydrobenzaldehyde, as produced in the liquid phase reaction, was converted to its semicarbazone and recrystallized three times. It then melted at $158-162^{\circ}$. A mixed melting point of $158-162^{\circ}$ showed that the materials were identical.

Although acrolein is stable, cyclopentadiene undergoes slow polymerization below 200° . At this temperature, however, it is stable. In order to calculate velocity constants below this temperature, it is necessary to know the rate of this side reaction. Accordingly six runs from $78-183^{\circ}$ were made using cyclopentadiene alone and second order velocity constants calculated. Since this reaction was slow, the experiments did not actually justify the assumption that the rate was second order; but this will be established in a paper soon to be published from this Laboratory. Though the correction amounted to only 4-10% (within the experimental error of measurement) it was always made. The assumption made in applying the correction, that these two reactions proceed independently of one another, would probably not be justified if either one were a chain reaction. The rate equation was not integrated, but was used in the differential form.

The second order constants calculated in this way were never constant during the whole course of the reaction. At temperatures above 166° , the constants fell off; below 140° , they increased. In Table I is given a detailed calculation of run number 2. The first two columns give the pressures of acrolein and cyclopentadiene at the initial

(8) For further information concerning the preparation of these samples of butadiene see Kistiakowsky, *et al.*, THIS JOURNAL, 58, 147 (1936).

point of a time increment. Columns 3 and 4 give the magnitude of this time and of the corresponding pressure increment. In column 5 is given the calculated increase in pressure of dicyclopentadiene which occurs during this time, while the last column gives the velocity constant.

TABLE I
ACROLEIN AND CYCLOPENTADIENE
Sample Calculation. Run 2

$P_{ac.}$ mm.	$P_{cyc.}$ mm.	Δt sec.	Δp_v mm.	Δp_d mm.	$k \times 10^6$ $mm.^{-1} sec.^{-1}$
237.0	191.0	57	4.0	0.2	1.6
233.1	186.9	126	8.4	.5	1.52
225.0	178.2	186	10.9	.7	1.45
214.4	167.0	125	6.6	.4	1.43
208.0	160.2	154	7.7	.5	1.47
200.6	152.0	202	9.2	.5	1.48
191.6	142.6	218	8.8	.5	1.47
183.1	133.5	268	9.8	.5	1.51
173.5	123.5	321	10.0	.5	1.47
163.8	113.2	398	10.5	.6	1.46
153.6	102.4	480	10.4	.5	1.43
143.5	91.8	633	10.9	.6	1.37
132.9	80.6	895	11.1	.6	1.22
122.1	69.2	1114	10.0	.6	1.13
112.4	58.9	1809	10.2	.6	.92
102.5	48.4	3094	10.0	.7	.71
92.8	38.1	5220	6.7	.8	.37
86.5	31.1	7200	3.2	.7	.12

A summary of the results obtained over the entire temperature range is given in Fig. 1. Percentage reaction is plotted along the abscissa and the ratios k/k_0 are plotted as ordinates. Here k is the constant corresponding to a given per cent. reaction and k_0 is the initial velocity constant. This initial value had been previously obtained by graphical extrapolation. At high temperatures the constants fall off more rapidly than at low temperatures, due to the increasing rate of the reverse reaction. The effect of pressure on the rate of falling off of the constants is illustrated in runs 3 and 4 at temperatures of 209.8 and 209.9°, respectively. The total initial pressures are 86.8 and 183.1 mm. The constants fall off more rapidly in run 3 than in run 4. This is what is to be expected if the disturbing influence is due to the reverse reaction.

The dependence of the value of the initial velocity constants upon the initial pressure can be read from Table II. This, as well as similar tables for other reactions here described, contains all experiments performed except those in which leaky valves and similar mishaps made a calculation of the results impossible. In the first column

is given the number of the run, column 2 gives the temperature in degrees centigrade, columns 3 and 4 give the initial pressures of acrolein and cyclopentadiene in mm., respectively, column 5 gives the extrapolated value of the velocity constant, column 6 the value of the calculated velocity constant, and the final column notes whether a packed or empty reaction flask was used. In the packed flask the surface-volume ratio was increased by a factor of 6 over that of the empty one.

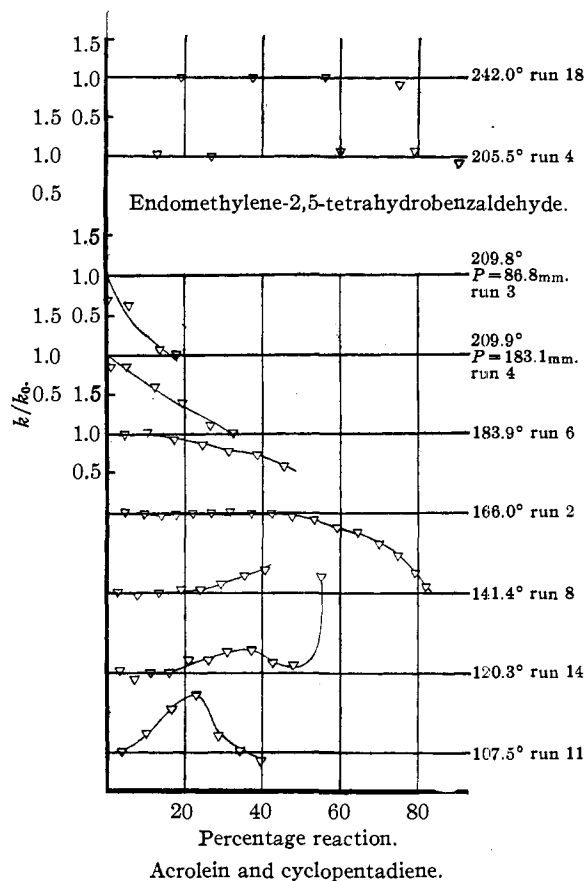


Fig. 1.

This table shows that the initial second order constants are independent of the pressure and also that the increased surface of the packed flask causes no change in the rate of the reaction. In runs 3 and 4 acrolein was admitted to the reaction vessel before the cyclopentadiene, while in runs 12 and 13 the order was reversed. No significant change in the velocity constants was observed. Further indication that the rate is second order will be obtained when the data on the reverse reaction are discussed. The reverse reaction is of the first order.

At temperatures of 141° and below, the velocity

TABLE II
ACROLEIN AND CYCLOPENTADIENE
Summary of Data

Run	T., °C.	P ac. mm.	P cyc. mm.	k expt., cc. mole ⁻¹ sec. ⁻¹	k calcd., cc. mole ⁻¹ sec. ⁻¹	Comment
4	209.9	98.3	84.8	210	196	Empty
3	209.8	44.8	42.0	196	196	Empty
12	205.1	117.6	51.7	143	167	Packed
13	204.1	167.8	90.8	164	162	Packed
6	183.9	163.9	114.0	74	80	Empty
7	183.8	98.8	56.1	71	80	Empty
5	167.0	99.7	137.8	38	42	Empty
2	166.0	237.0	191.0	40	40	Empty
1	147.0	209.1	228.7	18	18	Empty
8	141.4	188.8	189.1	13	14	Empty
14	120.3	362.5	176.6	5.4	5.3	Packed
11	107.5	204.2	249.4	3.1	2.8	Empty
15	92.5	302.6	291.2	1.4	1.2	Packed
9	78.0	258.4	328.3	1.0	(0.51)	Empty
10	78.0	230.9	215.8	0.98	(.51)	Empty

constants increase with per cent. reaction. Furthermore, as the temperature diminishes, this increase becomes more pronounced at smaller percentage reaction. At 120.3° k/k_0 goes through a hump at 35% reaction, while at 107.5° this hump

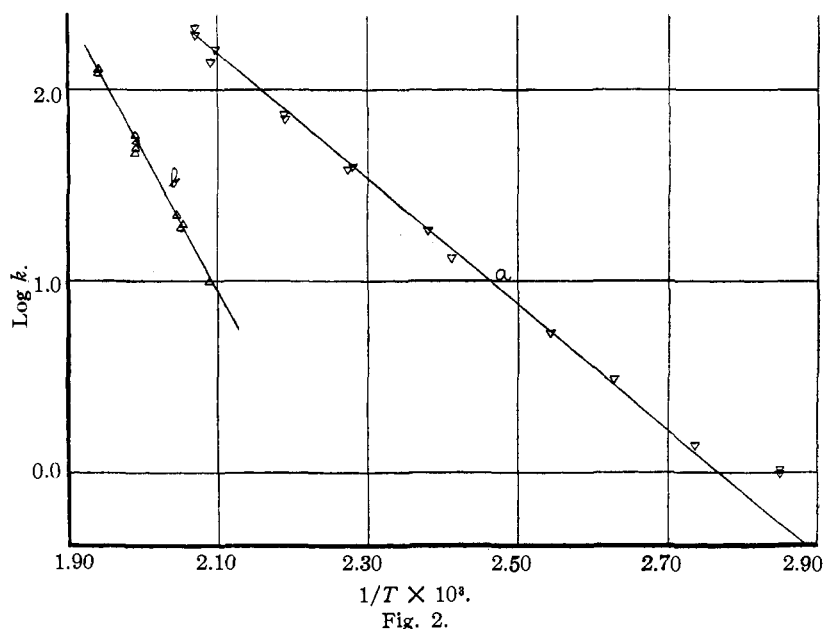


Fig. 2.

is more pronounced and corresponds to 25% reaction. The difficulty is no doubt due to the fact that endomethylenetetrahydrobenzaldehyde separates out as a liquid at these temperatures. If the presence of the liquid had no influence in the rate of reaction, one would expect the constants to double in value. In run 14 at 120.3° the con-

stants ultimately increased to about ten times their initial value. (This is not shown on the graph.) The kinetics of the reaction apparently undergo a marked change when the liquid phase appears and therefore runs made below 100° have little value.

A plot of the logarithms of the initial constants against the reciprocal of the absolute temperature is shown in Fig. 2, curve (a). The points fall fairly well on a straight line represented by the equation

$$k = 1.50 \times 10^9 e^{-16,200/RT} \text{ cc. moles}^{-1} \text{ sec.}^{-1}$$

which was used to calculate the values of Table III. The value for the activation energy is probably accurate to 1000 cal.

Decomposition of Endomethylenetetrahydrobenzaldehyde.—The endomethylenetetrahydrobenzaldehyde was distilled into a trap. In order to boil the material into the furnace, it was heated with an oil-bath to 150° (200° was too hot and caused too much decomposition). Acrolein and cyclopentadiene produced by the decomposition during this heating were pumped off and the material then admitted into the reaction flask.

Since the reaction is very fast and because of the decomposition of endomethylenetetrahydrobenzaldehyde while being boiled into the reaction flask, it was impossible to obtain the reactant's initial pressure. The procedure was to measure the total initial pressure as quickly as possible and note the time. Then pressure-time readings were taken until the reaction was complete. By assuming complete decomposition—which is admissible because of low pressures used—one can calculate the partial pressure of endomethylenetetrahydrobenzaldehyde at the initial time. First order velocity

constants were calculated from the integrated equation.

In Fig. 1 are shown the plots of the ratio k/k_{av} against per cent. reaction. k_{av} is the average value of k for the run, and k is the constant obtained at a given per cent. reaction. Table III gives a summary of the data obtained. The

TABLE III
ENDOMETHYLENETETRAHYDROBENZALDEHYDE
Summary of Data

Run	T., °C.	$P(i)$, mm.	$P(o)$,	$k \times 10^4$ (expt.) sec. ⁻¹	$k \times 10^4$ (calcd.) sec. ⁻¹
16	242.0	21.6	6.0	13	12.3
17	242.0	21.4	7.4	12	12.3
18	242.0	20.0	6.4	12	12.3
1	229.6	60.1	11.9	5.4	5.5
2	229.6	20.8	7.5	4.7	5.5
9	229.4	15.1	10.3	5.7	5.5
12	229.3	20.2	8.1	4.9	5.4
14	229.5	27.5	10.9	5.3	5.5
15	229.5	18.9	9.1	5.7	5.5
19	216.0	29.6	16.7	2.25	2.15
21	215.3	20.1	8.4	1.9	2.0
20	215.1	27.3	13.9	1.9	2.0
6	214.0	63.9	36.1	2.0	1.9
3	205.5	37.7	7.2	1.0	1.9
4	205.5	63.8	12.3	1.0	1.0
5	191.5	54.7	27.5 } 53.5 }	0.5 } .25 }	(0.35)

column under $P(i)$ gives the initial total pressures in mm. and the column under $P(o)$ gives the initial pressure of endomethylenetetrahydrobenzaldehyde. The calculated velocity constants were obtained from the equation

$$k = 2.2 \times 10^{12} e^{-33,600/RT} \text{ sec.}^{-1}$$

Aside from giving good constants during a run, further proof that the reaction is first order is given by the fact that these constants are independent of the initial pressure. There is no evidence of any falling off of the rate at pressures as low as 15 mm.

All of the experiments were made in the empty reaction vessel. Run 5 was made at a temperature low enough to permit the reverse reaction to be appreciable. One hundred per cent. decomposition did not occur. If one assumes this, the calculated initial pressure of endomethylenetetrahydrobenzaldehyde will be too small and the corresponding velocity constants will be too large. Since the velocity of the reaction is slow, one could get the initial pressure by extrapolating back to the initial time, if no decomposition occurred in the trap during admission. Otherwise one obtains an initial pressure which is too large and constants which are too small. The true constants should lie between these. The two constants obtained in this way are given in the table and it is seen that the calculated constant is about the average of these two. This run was not used in calculating the activation energy.

A plot of the logarithm of $k \times 10^4$ against $1/T$

is given in Fig. 2, curve (b). Because of the small temperature interval, the value for E cannot be very accurate; but it is thought that it is not in error by more than 1500 cal. To extend the temperature range, one would have to work at lower pressures than those for which the present apparatus was designed.

Acrolein and Butadiene.—Acrolein and butadiene react at a measurable rate in the temperature range 155–330°. At these temperatures the product is gaseous and stable, thus making the experimental results easier to interpret than was the case with acrolein and cyclopentadiene. The only complicating factor was the existence of a slow side reaction, the polymerization of butadiene. The experimental procedure was the same as that previously used. The two samples of butadiene were pure and a bulb-to-bulb distillation was used only to remove dissolved air. Sample H was used in runs 1 through 6 and D in runs 7 through 15. Both samples gave similar results.

The nature of the product formed was established as before. The semicarbazone melted at 152–154° after being recrystallized once out of aqueous methyl alcohol. The temperature of melting of the material formed in a liquid phase reaction is reported by Diels and Alder to be 153–154°. If the reacted gases after a run were condensed out in a clean trap, they would form clear colorless liquids. This was true of all the reactions studied.

In making calculations of second order constants, the differential form of the equation was again used. The velocity constants giving the rate of formation of the dimer of butadiene were calculated from Vaughan's equation. The correction was 1% at low temperature and 5% at high temperature, unless a large excess of butadiene was used.

Two runs on the polymerization of butadiene were made and compared with the rate calculated from Vaughan's equation. The data are given in the following table.

Temp., °C.	k (expt.) mm. ⁻¹ sec. ⁻¹	k (calcd.) mm. ⁻¹ sec. ⁻¹
290.7	9.6×10^{-8}	6.5×10^{-8}
282.4	7.1×10^{-8}	4.0×10^{-8}

The measured values are much larger than the calculated ones. The reason for the discrepancy is not known. An error of 10° in the temperature scales or a difference in purity of the samples of 20% would account for it. Unfortunately no

further runs were made. This makes uncertain the correction made for the side reaction, and it appears that the true correction may be nearly twice as large as the one made. This would change the velocity constants about 5%.

TABLE IV
ACROLEIN AND BUTADIENE
Sample Calculation, Run 5

P ac., mm.	P but., mm.	Δt , sec.	Δp_t , mm.	$\Delta p_{poly.}$, mm. mm. ⁻¹ sec. ⁻¹	$k \times 10^7$ mm. mm. ⁻¹ sec. ⁻¹
418.2	240.0	63	6.1	0.2	9.6
412.3	233.7	118	10.7	.3	9.5
401.9	222.7	203	17.3	.5	9.9
385.1	204.9	158	11.9	.3	9.7
373.5	192.7	203	14.1	.3	10.0
359.7	178.3	180	11.0	.3	9.7
349.0	167.0	220	12.2	.3	9.8
337.1	154.5	229	10.8	.3	9.3
326.6	143.4	253	11.3	.2	9.9
315.5	131.9	361	13.4	.3	9.4
302.4	118.2	443	13.9	.3	9.4
288.8	104.0	463	12.0	.2	9.2
277.0	91.8	509	11.1	.2	9.1
266.1	80.5	690	12.6	.2	9.3
253.7	67.7	926	12.4	.2	8.7
241.5	55.1	1061	11.3	.1	9.1
230.3	43.7	1288	9.8	.1	8.7
220.6	33.8	1747	8.9	.1	8.0
211.8	24.8	3440	10.7	.1	7.7

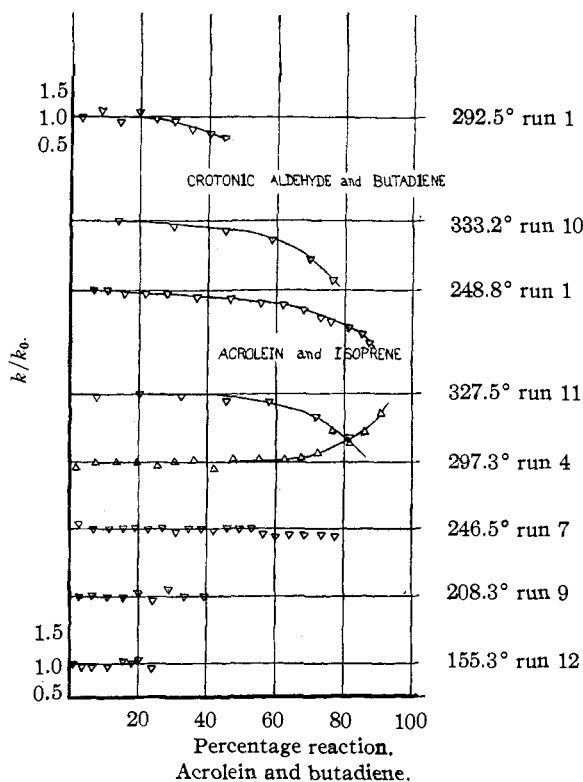


Fig. 3.

Table IV gives a complete calculation of run 5; this is similar to Table I. Figure 3 illustrates the experimental results. As before, k/k_0 is plotted against per cent. reaction. It is seen that good second order constants are obtained. In run 4 twice as much butadiene was present as acrolein, so near the end of the reaction the correction for the side reaction became large. The velocity constants obtained at 330° were erratic and fell off after about 50% reaction. At this temperature acrolein begins to decompose; also the reaction may begin to reverse. The velocity of the reaction at 155° is quite slow. Run 12 was extended over a period of two days.

Table V summarizes the data obtained. Runs 4, 10, 3, and 5 show that the rate is proportional to the product of the amounts of each reactant over a pressure range of 650–150 mm. Also the reaction is homogeneous. In run 7 butadiene was admitted to the furnace first. Apparently the order of mixing the two gases makes no difference in the rate of reaction.

TABLE V
ACROLEIN AND BUTADIENE
Summary of Data

Run	T., °C.	P ac., mm.	P but., mm.	k expt., cc. mole ⁻¹ sec. ⁻¹	k calcd., cc. mole ⁻¹ sec. ⁻¹	Comment
6	331.5	213.2	94.0	109	111	Packed
15	330.8	222.4	99.2	81	110	Empty
14	328.5	114.7	43.3	87	102	Empty
11	327.5	99.6	48.0	94	100	Empty
4	297.3	212.3	435.5	45.9	41.6	Packed
10	295.8	102.3	52.9	36.8	38.8	Empty
3	295.1	193.8	175.8	38.6	38.8	Packed
5	291.2	418.2	240.0	34.2	34.5	Packed
7	246.5	428.3	302.5	7.2	7.57	Empty
1	244.2	272.0	297.7	6.8	6.98	Packed
2	243.8	473.9	245.8	6.8	6.86	Packed
9	208.3	461.4	274.6	1.63	1.66	Empty
8	207.3	453.0	286.9	1.53	1.60	Empty
13	155.7	382.7	365.4	0.135	0.130	Empty
12	155.3	403.2	328.4	.138	.132	Empty

A plot of the logarithm of k (expt.) against $1/T$ is given in Fig. 4, curve a. The equation expressing the straight line is

$$k = 1.46 \times 10^9 e^{-19,700/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

If one uses a correction for the side reaction which is just twice as large as given by Vaughan's equation, the best fit is obtained with the Arrhenius equation

$$k = 1.05 \times 10^9 e^{-19,400/RT}$$

The change of 300 cal. in the activation energy can hardly be greater than the experimental error.

Crotonic Aldehyde and Butadiene.—The reaction between crotonic aldehyde and butadiene is a slow one in the temperature range 250–300°. Preliminary experiments with crotonic aldehyde showed that it was stable at temperatures up to 325; above this temperature, it begins to decompose.

In establishing the nature of the product of the reaction, care had to be taken to distil out all the unreacted crotonic aldehyde. This substance has a boiling point 50° higher than acrolein and will form a crystalline semicarbazone melting at 196–198°. The product of the reaction formed a semicarbazone which melted at 163–167° after one recrystallization. A small amount of methyl-6- Δ^3 -tetrahydrobenzaldehyde was made according to the method of Diels and Alder⁷ and purified by a trap distillation. It formed a semicarbazone melting at 166–168° after one recrystallization. A mixed melting point of the two semicarbazones gave 163–168°. Diels and Alder reported that the semicarbazone melts at 168°.

Even though all runs were made with a large excess of crotonic aldehyde present, the correction for the polymerization of butadiene amounted to about 25%. Because of this fact and that only a small temperature range was used, the results were not very accurate.

TABLE VI
CROTONIC ALDEHYDE AND BUTADIENE
Summary of Data

Run	T , °C	P cro., mm.	P but., mm.	k expt., cc. mole ⁻¹ sec. ⁻¹	k calcd., cc. mole ⁻¹ sec. ⁻¹	Comment
7	299.6	392.6	91.6	3.8	3.6	Empty
1	292.5	404.0	161.0	2.8	2.8	Packed
6	279.4	410.1	143.8	1.5	1.8	Empty
2	275.3	393.4	223.5	1.6	1.5	Packed
5	249.5	440.1	151.3	0.55	0.56	Empty
4	242.0	415.8	175.7	.38	.41	Empty

A plot of k/k_0 against per cent. reaction is given in Fig. 3 and the summary of the data obtained is given in Table VI. The velocity constant giving the rate of formation of the dimer of butadiene

was calculated from Vaughan's equation. Figure 4, curve b, gives a plot of the logarithm of k against $1/T$. Arrhenius' equation expressing the straight line is

$$k = 9.0 \times 10^9 e^{-22,000/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

If one uses a value of the velocity constant for the polymerization of butadiene just twice as large as the calculated one and recalculates the results, the resulting Arrhenius equation is

$$k = 2.5 \times 10^9 e^{-21,000/RT}$$

This change is within the rather large experimental error.

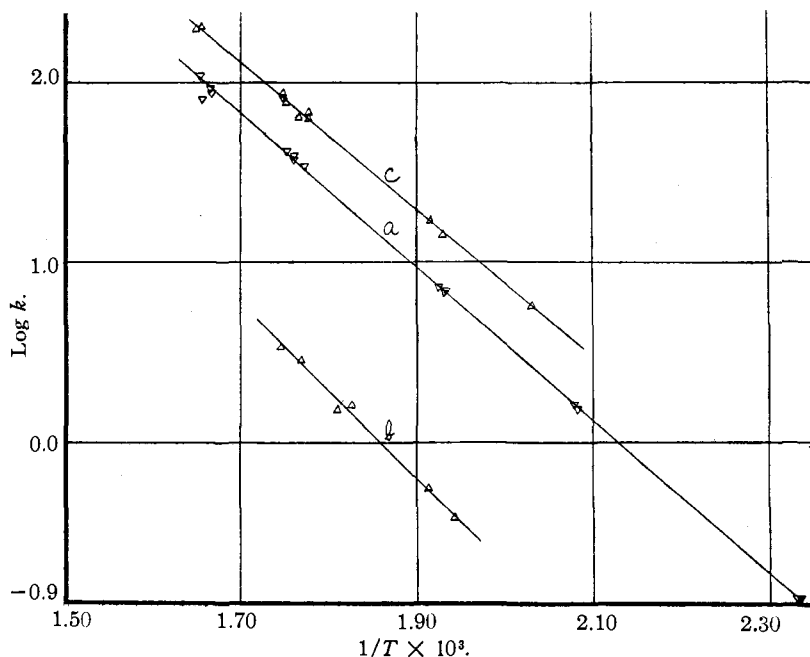


Fig. 4.

Acrolein and Isoprene.—The rate of the reaction of acrolein with isoprene is about twice as great as the rate of the corresponding reaction with butadiene. The reaction was studied in the temperature interval 218–333°. As the isoprene was of unknown purity, only one-third of the material was preserved in each bulb-to-bulb distillation. In other respects the experimental procedure was the same as that employed in the other reactions.

The product of the gas phase reaction formed a semicarbazone which melted at 145.5–146° after two recrystallizations. The value reported by Diels and Alder for the semicarbazone of methyl-3(4[?])- Δ^3 -tetrahydrobenzaldehyde is 146°.

At 325° isoprene polymerizes at about the same rate as does butadiene. Accordingly the correction made for this side reaction was only half as

large. It amounted to 1 to 5% if acrolein was present in excess. Only one run was made to test the rate of the polymerization of isoprene. This was done at 245.3° where the reaction was very slow. The constant obtained for about 6% reaction was 2×10^{-8} mm.⁻¹ sec.⁻¹. At the same temperature an extrapolation of the results of Vaughan gives 1×10^{-8} mm.⁻¹ sec.⁻¹. This discrepancy is to be expected, since, according to Vaughan, the initial rate is greater than the rate obtained after 10% reaction.

The velocity constants giving the rate of formation of the dimer of isoprene were calculated from Vaughan's data. If one doubles the magnitude of this correction, the result is to change the energy of activation by 100 cal. That the correction applied is necessary and is of the correct order of magnitude is indicated from the results of run 4. Here three times as much isoprene was present as acrolein, and the correction amounted to 12%. If one uses a correction of 24%, one obtains a constant that is abnormally low when compared with other runs made in the same temperature region.

In Fig. 3 are given the graphs of k/k_0 against per cent. reaction. It is seen that this ratio falls off and does so more rapidly at high temperatures. This may be due to the existence of the reverse reaction. As was the case of the other reaction, this one proved to be homogeneous and to possess a rate independent of the order in which the reacting gases were admitted to the furnace. A complete summary of the data obtained is given in Table VII. The calculated values of the velocity constant were obtained from the expression

$$k = 1.02 \times 10^9 e^{-13,700/RT} \text{ cc. moles}^{-1} \text{ sec.}^{-1}$$

A plot of the logarithm of k against $1/T$ is shown in Fig. 4, curve c.

TABLE VII
ACROLEIN AND ISOPRENE
Summary of Data

Run	T., °C.	P ac., mm.	P iso., mm.	k , expt., cc. mole ⁻¹ sec. ⁻¹	k , calcd., cc. mole ⁻¹ sec. ⁻¹	Comment
10	333.2	104.3	48.4	200	210	Packed
9	330.9	58.7	39.0	203	200	Packed
7	299.2	227.0	142.0	84	84	Packed
3	299.0	410.0	213.2	85	84	Empty
8	297.5	50.5	53.0	77	80	Packed
4	293.4	80.0	251.8	65	70	Empty
6	291.8	47.6	44.1	69	67	Empty
5	290.5	106.5	63.2	64	65	Empty
1	248.8	431.8	155.4	17	17	Empty
2	244.8	249.8	255.0	14	15	Empty
11	218.7	280.2	339.9	5.7	5.7	Packed

Discussion of Results

In Table VIII is given a summary of the activation energies and the A -factors obtained for these reactions.

TABLE VIII

Association reaction	E cal.	$A \times 10^{-9}$, cc. moles ⁻¹ sec. ⁻¹	K_{200° , cc. moles ⁻¹ sec. ⁻¹
Acrolein and cyclopentadiene	15,200	1.50	153
Acrolein and isoprene	18,700	1.02	2.3
Acrolein and butadiene	19,700	1.46	1.2
Crotonic aldehyde and butadiene	22,000	0.90	0.062
Decomposition reaction		$A \times 10^{-12}$, sec. ⁻¹	K_{200° , sec. ⁻¹
Endomethylenetetrahydrobenzaldehyde	33,600	2.2	0.0067

In order to facilitate a comparison of the different rates, the velocity constants at 200° are also tabulated. The diminishing rate as read from the top of the table to the bottom is in qualitative agreement with the research of Diels and Alder⁷ on the liquid phase reaction.

Also the fact that the acrolein-cyclopentadiene reaction is reversible is in agreement with the organic chemistry of these compounds. As has been mentioned before, when the product of a diene synthesis contains a bridged ring, then it is rather unstable and can be decomposed readily by heating. When the reaction results in the formation of a simple six-membered ring, there is no indication of the reverse reaction taking place at the temperature of 300°. The falling off of the constants at 330° may be due, however, to this reverse reaction. While the slow decomposition of acrolein, which occurs at this temperature, could cause the same behavior, it is more reasonable to suppose, in analogy with the behavior of endomethylenetetrahydrobenzaldehyde, that the simple six-membered ring aldehydes also reverse at higher temperatures. This supposition is supported by the fact that isoprene can be made out of limonene,⁹ and cyclohexene¹⁰ can be decomposed into ethylene and butadiene. Both these reactions can be regarded as the reverse of a Diels-Alder reaction.

From a knowledge of the direct and reverse reactions, the equilibrium constant for reaction A can be expressed as a function of the temperature. Expressed in units of atmospheres it is

$$-RT \ln K = \Delta F^\circ = -19,300 + 37.5T$$

(9) Harries and Gottlob, *Ann.*, **383**, 228 (1911).

(10) Kistiakowsky, *et al.*, unpublished work

For most first-order reactions the kinetic A -factors are around 10^{13} to 10^{14} sec.⁻¹. The observed A -factor for the decomposition of endomethylenetetrahydrobenzaldehyde is 2.2×10^{12} sec.⁻¹. This is only slightly smaller than the "normal" values. Besides, it is believed that the deviation may be due partly to the uncertainty in its determination. The explanation of some very low A -factors, as found for instance, for the nitrous oxide reaction,¹¹ has been given by Herzberg:¹² in order for the reaction to take place, the electronic state must change, and thus the process cannot take place adiabatically. The almost normal A -factor given by endomethylenetetrahydrobenzaldehyde indicates, however, that the electronic state does not change in the reaction. Accordingly, in the reverse reaction, no slowing down of the rate should occur on that account.

Table VIII shows that, within experimental error, the differences in the rates of these association reactions are due to changes in the activation energy. The A -factors are all of the same order of magnitude and are exceptionally small. According to the collision theory, the A -factor is simply the number of collisions between reacting molecules at unit concentration. Assuming a molecular diameter of 5×10^{-8} cm. and a temperature of 500°K. this number is, in moles per cc. per sec., about 10^{14} . The experimental A -factors are 1 to 1.5×10^9 . To take care of this discrepancy, a steric factor of 10^{-5} would have to be assumed.

The A -factors are even smaller than the number of triple collisions occurring. At a total pressure of 15 mm. and at 500°K., one calculates that the number of molecules of endomethylenetetrahydrobenzaldehyde formed per sec. per cc. is 1.0×10^{13} . Under the same conditions, the total number of collisions multiplied by $e^{-15,200/RT}$ is 3.0×10^{13} . The fraction of these double collisions which take place within molecular distance of a third body is roughly given by the expression: $N_{III}/N_{II} = \delta/\lambda$ where δ is the molecular diameter and λ the mean free path at 15 mm. pressure. This fraction has an estimated value 2×10^{-4} . Accordingly, the number of double collisions $\times e^{-15,200/RT}$ which take place within molecular distance of a third molecule is

$$N_{III} = N_{II} \times 2 \times 10^{-4} = 2 \times 10^{13} \times 2 \times 10^{-4} = 4 \times 10^{14}$$

(11) Volmer and Kummerow, *Z. physik. Chem.*, **9B**, 141 (1930); Nagasko and Volmer, *ibid.*, **10B**, 414 (1930).

(12) Herzberg, *ibid.*, **17B**, 68 (1932).

The reaction is thus much slower than the rate of "triple" collisions with sufficient energy and the discrepancy increases with increasing pressure because of the observed second-order rates.

The explanation of some slow reaction rates has recently been sought in the statistical mechanical expression giving the entropy change.^{13,14,15} For the reaction $M_2 + M_3 \rightarrow M_1$, which interests us here, we shall use the form of the theory developed by Rice and Gershinowitz.¹⁴ They find that if one assumes that the probability of decomposition is independent of the translational and rotational states of the molecules, then the rate of association will not equal the number of collisions between activated molecules. Instead, the rate will be slower. The reason for this is that, during the reaction, certain rotational degrees of freedom in the reacting molecules must pass over into vibrational degrees of freedom in the product molecule. In their hypothesis of "exact orientation" they assume that these rotations will have to be "frozen out" to an amount equal to the difference in entropy which they would contribute as rotations and that which they would contribute as vibrations, meaning that only molecules in certain rotational stages can undergo reaction.

In arriving at these conclusions Rice and Gershinowitz assumed that the speed of reaction did not depend on the rate with which energy is removed from the associated molecule. Further, the reaction must go by an adiabatic process. Diels-Alder reactions seem to satisfy these conditions.

According to this theory, the A -factors of the dissociation and association reactions are given by the following expressions

$$A_1 = \frac{ekT}{E_1' h} \text{ sec.}^{-1} \quad (1)$$

$$A_2 = \frac{eB_1 C_1 E_1''}{B_2 C_2 E_2 B_3 C_3 E_3} \frac{kT}{h} \text{ cc. molecules}^{-1} \text{ sec.}^{-1} \quad (2)$$

In these equations the subscript 1 refers to the associated molecule, while the subscripts 2 and 3 refer to the associating molecules. The expressions for B , C , and E are

$$B = [(2\pi em'kT)/(h^2)]^{1/2} \\ = m^{3/2} \times 9.55 \times 10^{24} \text{ when } T = 500^\circ\text{K.}; \\ m \text{ is the gram molecular weight of the molecule.} \\ C = \frac{1}{\pi} \left(\frac{8\pi^3 e I' kT}{h^2 \sigma_1^2} \right)^{1/2} \left(\frac{8\pi^3 e I'' kT}{h^2 \sigma_2^2} \right)^{1/2} \left(\frac{8\pi^3 e I''' kT}{h \sigma_3^2} \right)^{1/2}$$

(13) Rodebush, *J. Chem. Phys.*, **1**, 440 (1933).

(14) Rice and Gershinowitz, *ibid.*, **3**, 853 (1934); Rice and Gershinowitz, *ibid.*, **3**, 479 (1935).

(15) Eyring, *ibid.*, **3**, 107, 497 (1935).

for an "unsymmetric top" molecule. I' , I'' , I''' are the three principal moments of inertia.

$$\left(\frac{8\pi^3 ekT}{h^2}\right)^{1/2} = 1.04 \times 10^{21} \text{ c. g. s. units when } T = 500^\circ \text{K.}$$

$$\ln E = \sum_j \left\{ \frac{h\nu_j}{kT} \times \frac{1}{e^{h\nu_j/kT} - 1} - \ln [1 - e^{-h\nu_j/kT}] \right\}$$

ν_j are the frequencies of the molecule and the summation extends over all frequencies.

In equation (1), E_1' contains a single frequency. This is roughly ascribed to the vibrations of those parts of M_1 which, upon decomposition, give M_2 and M_3 . The remaining vibrations of M_1 are contained in E_1 .

Since the vibrational frequencies of these molecules are not known, the assumption is made, in the following calculations, that the frequencies present in M_2 and M_3 are maintained in M_1 . Furthermore, the free rotation of the aldehyde group is neglected. This rotation will not be frozen out in the reaction. When association occurs, the six translational and six rotational degrees of freedom of M_2 and M_3 pass over into three translational, three rotational and six vibrational degrees of freedom in M_1 . One of these vibrational degrees of freedom is expressed in E_1' , and can be calculated from the dissociation rate. All other vibrations of M_1 , except the six new ones, will cancel with E_2 and E_3 . The resulting expression for A_2 is

$$A_2 = \frac{eB_1C_1E_{6\text{vib.}}}{B_2C_2B_3C_3} \frac{kT}{h}$$

For reaction A , the moments of inertia have been calculated to be approximately:

Endomethylenetetrahydrobenzaldehyde	Acrolein
C. g. s. units	C. g. s. units
$I_1' = 60 \times 10^{-39}$	$I_3' = 14 \times 10^{-39}$
$I_1'' = 40 \times 10^{-39}$	$I_3'' = 14 \times 10^{-39}$
$I_1''' = 20 \times 10^{-39}$	$I_3''' = 7 \times 10^{-39}$

Cyclopentadiene

$$\begin{aligned} I_2' &= 8 \times 10^{-39} \\ I_2'' &= 14 \times 10^{-39} \text{ c. g. s. units} \\ I_2''' &= 22 \times 10^{-39} \end{aligned}$$

In making these calculations, the following bonding distances and a tetrahedral angle of 110° were used.

$$\begin{aligned} \text{C}-\text{C} &= 1.5 \times 10^{-8} \text{ cm.} \\ \text{C}=\text{C} &= 1.4 \\ \text{C}-\text{H} &= 1.1 \\ \text{C}=\text{O} &= 1.3 \end{aligned}$$

A numerical calculation gives, at a temperature of 500°K.

$$A_2 = E_{6\text{vib.}} \cdot 2.28 \times 10^6 \text{ cc. moles}^{-1} \text{ sec.}^{-1}$$

This must equal 1.50×10^9 , or

$$E_{6\text{vib.}} = (1.50 \times 10^9) / (2.28 \times 10^6)$$

In order to satisfy this relation, the average frequency of these five vibrations must be 122 cm.^{-1} .

From the expression for A_1 , the frequency of the sixth vibration can be calculated.

$$E_1 = \frac{ekT}{A_1 h} = \frac{2.78 \times 10^{13}}{2.2 \times 10^{12}} = 12 \text{ or } \tilde{\nu}_6 = 80 \text{ cm.}^{-1}$$

Considering the approximations made in these calculations, the values for the frequencies are reasonable, although perhaps too low because some of them, at least, must be stretching vibrations; and the theory is seen to be capable of explaining the small A -factor for this association reaction in an almost quantitative manner.

Cyclopentadiene differs from butadiene in that it can have no internal rotations. In the case of butadiene, there exists the possibility of "free rotation" about the central carbon-carbon single bond. It is interesting to calculate, according to the theory, whether the presence or absence of "free rotation" in butadiene will alter the A -factor for reaction B.

An "ethane top"¹⁶ molecule will be used for the "free rotation" calculation. This is a very crude approximation because butadiene cannot undergo a symmetrical rotation about the central C-C bond. On the basis of this assumption C becomes

$$C = \frac{1}{\pi} \left(\frac{8\pi^3 e I' kT}{h^2 \sigma_1^2} \right)^{1/2} \left(\frac{8\pi^3 e I'' kT}{h^2 \sigma_2^2} \right)^{1/2} \left(\frac{8\pi^3 e I''' kT}{h^2 \sigma_3^2} \right)^{1/2} \left(\frac{8\pi^3 e I'''' kT}{h^2 \sigma_4^2} \right)^{1/2}$$

This differs from the expression for C in case of a "rigid top" molecule by a factor of $1.04 \times 10^{21} \times I^{1/2}$.

For butadiene the following approximate moments of inertia were used

$$\begin{aligned} I_2' &= I_2'' = 14 \times 10^{-39} \text{ "end over end" moments} \\ I_2''' &= I_2'''' = 3.6 \times 10^{-39} \text{ "free rotation" moments} \end{aligned}$$

In case of a rigid top molecule, we have the following moments

$$\begin{aligned} I_2' &= 14 \times 10^{-39} \\ I_2'' &= 14 \times 10^{-39} \\ I_2''' &= 7 \times 10^{-39} \end{aligned}$$

Numerical calculation gives for the two cases

$$\begin{aligned} 1/C_2 &= 1.7 \times 10^{-8} \text{ "free rotation"} \\ 1/C_2 &= 7.6 \times 10^{-7} \text{ "rigid top molecule"} \end{aligned}$$

If a "free rotation" exists, then seven new vibrations will be formed upon reaction. The internal rotation will only have to be "frozen out" to the extent of forming the new seventh vibration. This will reduce somewhat the inhibiting effect it has on the reaction.

(16) Mayer, Bruinauer and Mayer, *THIS JOURNAL*, **55**, 37 (1933).

In order to calculate the E for this one vibration, the assumption will be made that its frequency is 122 cm.^{-1} , the value for the average frequency formed in endomethylenetetrahydrobenzaldehyde. This gives E a value of 7.6. For "free rotation" then

$$E/C_2 = 1.7 \times 10^{-8} \times 7.6 = 1.3 \times 10^{-7}$$

The presence of the "free rotation" will thus reduce the rate by approximately a factor of 5. If instead of rotation, a torsional vibration of low frequency is assumed, the difference of the two results is even less. Because of experimental errors and the approximate nature of the calculation, no decision as to the existence of internal "free rotation" in butadiene can evidently be made.

A calculation identical to that made for the cyclopentadiene reaction also was made for the butadiene reaction. For this purpose the products of these two reactions were assumed to have the same moments of inertia. If no "free rotation" is assumed, an average frequency of 190 cm.^{-1} for the five vibrations formed will account for the rate of the reaction. The assumption of "free rotation" requires that six vibrations have an average frequency of 128 cm.^{-1} .

These crude calculations show that the theory of "exact orientation" requires that there should be little or no difference in the A -factors for the butadiene and cyclopentadiene reactions. And since the masses and moments of inertia of the molecules involved in reactions C and D are nearly the same as those involved in reactions A and B, their A -factor should be nearly the same in agreement with experimental results.

A difficulty arises, however, as pointed out already by Rice and Gershinowitz, in interpreting the results of Vaughan on butadiene and isoprene polymerizations. Their A -factors are far too large for the theory, if the mechanism of the reaction is that of the diene synthesis, that is, the

formation of a closed six-membered ring structure. In an attempt to understand the difference, one has to consider further that in these reactions, contrary to the "regular" Diels-Alder cases, the association does not stop at a dimeric stage but, particularly in the liquid phase, proceeds further to a formation of large polymers. One obtains, perhaps, an understanding of all these facts and also of the much higher activation energies observed in the two reactions when it is assumed that the first step of the association is not the formation of a ring system typical of the Diels-Alder reactions. This problem, however, will be taken up more in detail in another communication.

Summary

The kinetics of the gas phase reactions have been studied with four of the simplest Diels-Alder associations. The reactions were found to be of the second order, homogeneous and only slightly complicated by side processes.

The results can be expressed by the following equations

Acrolein and cyclopentadiene:	$k = 1.50 \times 10^9 e^{-15,200/RT}$
Acrolein and isoprene:	$k = 1.02 \times 10^9 e^{-18,700/RT}$
Acrolein and butadiene:	$k = 1.46 \times 10^9 e^{-19,700/RT}$
Crotonic aldehyde and butadiene:	$k = 0.90 \times 10^9 e^{-22,000/RT}$

The product formed in the first of the above reactions, endomethylenetetrahydrobenzaldehyde is unstable at elevated temperatures. Its decomposition was studied and was found to be of the first order. The rate is given by the following equation

$$k = 2.2 \times 10^{12} e^{-33,600/RT}$$

The theoretical treatment of association reactions in the form developed by Rice and Gershinowitz can be applied to these reactions. The results are very reasonable, showing that the theory is correct essentially, although somewhat slower rates would have fitted the theory even better.

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