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Studies in Gaseous Polymerizations

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EARLIER work on simple gaseous polymerizations¹⁻⁹ has clearly shown that association reactions of lower dienes follow simple kinetic laws and are amenable to treatment by the newer statistical theories of reaction rates.

The present contribution describes efforts to extend the detailed knowledge of these reactions and also contains a more comprehensive discussion of the reaction mechanism than has been possible with the meager kinetic data heretofore available.

EXPERIMENTAL DETAILS

All observations on the rates of association reactions were made with static systems by following pressure changes and by occasionally analyzing the products. For pressure measurements quartz spiral gauges were employed. In handling compounds with higher boiling points, heated metal valves with Sylphon bellows or heated all-glass valves with silver-chloride-coated seats were used exclusively. Oxygen was kept out of the system by repeated evacuations without intervening admission of air and by careful fractionation of the reactants in vacuum. Unless stated otherwise, no other precautions were employed. Air furnaces, electrically heated and manually controlled, were used except in the work on the association of cyclopentadiene for

which an oil bath was employed. Temperatures were read with thermocouples calibrated against a platinum resistance thermometer.

In studying the rate of polymerization of cyclopentadiene in the liquid phase freshly prepared cyclopentadiene, after repeated distillations in vacuum, was condensed in several small tubes which were then sealed off from the evacuating system. They were immersed in a thermostat for varying lengths of time and analyzed by determining their refractive index with a Pulfrich refractometer calibrated beforehand with known mixtures of monomer and dimer. The calibration gave a nearly linear relationship between the refractive index and the weight-concentration of the monomer. In working with solutions of cyclopentadiene in tetrahydronaphthalene, the former was distilled in vacuum into a sample of the solvent which had been previously boiled out in vacuum. The solution was forced by pure nitrogen into several tubes placed in a flask with their open ends, drawn into fine capillaries, pointing downwards. These ends were sealed off after the tubes were taken out of the system. This procedure was necessary because solutions distributed to reaction tubes and sealed off in vacuum became slightly nonuniform due to evaporation of cyclopentadiene and caused inconsistent results. The reaction was followed by withdrawing tubes after various heating periods and observing the refractive indices, this time using a Zeiss portable laboratory liquid interferometer. To calculate the rate constant of the liquid reaction in cc mole⁻¹ sec.⁻¹, the densities of the various mixtures were determined by the Westphal balance method and found to be additive. It was also found that the vapor pressure of the monomer obeyed Henri's law in dimer and in tetrahydronaphthalene mixtures, showing that these solutions are nearly ideal.

In differentiating between methyl acetylene and allene, the methyl acetylene was absorbed in a potassium iodo mercurate solution¹⁰ contained

¹ Perkin, *J. Soc. Chem. Ind.* **31**, 616 (1912).

² Lebedev, (a) *J. Russ. Phys. Chem. Soc.* **42**, 949 (1910); (b) *ibid.* **45**, 1249 (1913); (c) *Rev. gén. chim.* **18**, 102 (1918); (d) *J. Russ. Phys. Chem. Soc.* **45**, 1924, 1940 (1913).

³ Gapon, (a) *J. Russ. Phys. Chem. Soc.* **62**, 1325, 1395 (1930); (b) *ibid.* **63**, 496 (1931); (c) *Chem. J. Ser. A J. Allg. Chem.* **1** (63), 765 (1931); (d) *J. Gen. Chem. (U.S.S.R.)* **1**, 770 (1931).

⁴ Staudinger, (a) *Trans. Faraday Soc.* **32**, 98 (1936); (b) *Ber.* **46**, 2466 (1913).

⁵ Whitby, (a) and Galloway, *Can. J. Res.* **6**, 280 (1932); (b) and Crozier, *ibid.* **6**, 203 (1932); (c) and Macallum, *Trans. Roy. Soc. Can.* **22**, 39 (1928).

⁶ Krautz, Nantsov and Sovking, *Compt. rend. acad. sci. U.S.S.R.* **3**, 265 (1934).

⁷ Vaughan, (a) *J. Am. Chem. Soc.* **54**, 3863 (1932); *ibid.* **55**, 4109 (1933).

⁸ Rice and Gershinowitz, (a) *J. Chem. Phys.* **2**, 853 (1934); (b) *ibid.* **3**, 479 (1935).

⁹ Kistiakowsky and Lacher, *J. Am. Chem. Soc.* **58**, 123 (1936).

¹⁰ Hurd and Spence, *J. Am. Chem. Soc.* **51**, 3354 (1931).

in an analytical shaker¹¹ and a duplicate device containing 82.4 percent sulfuric acid was used for the allene. In preparing the dimerization product of 1,3-butadiene, a 12-liter reaction vessel was used and the product withdrawn from the flask by evacuation through traps so that the dimer collected was freed of unreacted butadiene.

COMPOUNDS

Styrene was obtained from Eastman Kodak Company and was distilled from bulb to bulb in vacuum to free it from polymers and was then distilled into the storage bulb of the apparatus.

Vinyl acetate was part of a sample used for the measurement of its heat of hydrogenation¹² and had been subjected to a careful distillation in a 15-ft. fractionating column.

Chloroprene was kindly presented to us by the duPont Company¹³ and was available as a 50 percent solution in naphtha, stabilized by catechol. Bulb to bulb distillations freed it from the solvent and stabilizing agent whereupon it was distilled into the storage bulb and kept in darkness.

Vinyl acetylene was also presented to us by the duPont Company and was in a 50 percent naphtha solution from which it was separated by bulb to bulb distillations.

Allene was part of a sample prepared for heats of hydrogenation measurements¹⁴ and was of a high degree of purity.

Methyl acetylene was prepared by debrominating 1,2-dibromopropane by means of a boiling solution of potassium hydroxide in *n*-butyl alcohol,¹⁵ and was purified by drying and bulb to bulb distillations in vacuum.

Cyclopentadiene was made by cracking pure dicyclopentadiene prepared from crude dicyclopentadiene obtained from Drs. Fraenkel and Landau of Germany. The method has been described elsewhere.¹⁴ Dicyclopentadiene melting from 31.7–32.0° was used to obtain the monomer.

¹¹ Chambers and Kistiakowsky, *J. Am. Chem. Soc.* **56**, 399 (1934).

¹² See a forthcoming publication from this laboratory for details.

¹³ We wish to thank Dr. A. S. Carter of the Jackson Laboratory for this material and also for the sample of vinyl acetylene.

¹⁴ Kistiakowsky, Ruhoff, Smith and Vaughan, *J. Am. Chem. Soc.* **58**, 146 (1936).

¹⁵ Tapley and Giesey, *J. Am. Pharm. Assn.* **15**, 115 (1926).

1,3-Pentadiene was part of a sample made for work on its heat of hydrogenation⁵⁰ and was of a high degree of purity.

2,3-Dimethyl butadiene-1,3 was also made for the calorimetric work.⁵⁰ Unfortunately, sample I, which was a part of the middle fraction from the 15-ft. still, was exhausted before the kinetic measurements were completed. Samples II and III represent fractions collected near the beginning of the distillation and are decidedly inferior, on the basis of their boiling ranges, to sample I. We are unable, however, to estimate the degree of their absolute purity.

1,3-Butadiene was prepared by cracking cyclohexene with a chromel cracking coil.¹⁴ It was purified by bulb to bulb condensation and solidification in vacuum.

EXPERIMENTAL RESULTS

Most of the compounds described in the preceding section showed behavior which made them unsuitable for kinetic studies below atmospheric pressure of the type here intended. Nevertheless, the results obtained will be described briefly, chiefly to spare others unnecessary experimental work.

Styrene is stable to about 400°, but at that temperature a slow reaction begins, accompanied by a decrease in pressure. Apparently, the reaction ceases after a small percentage pressure change. At a slightly higher temperature, 420°, an increase in pressure is observed, indicating the predominance of a decomposition reaction.

Vinyl acetate begins to decompose at about 360° and no temperature range has been found in which a measurable polymerization takes place at pressures below one atmosphere.

Chloroprene begins to polymerize at about 230° but at 260° decomposition becomes predominant. The pressure decreases much less than one would expect even for the formation of a dimer. Thus, at 447 mm initial pressure, the reaction apparently ceases when the pressure drops to about 324 mm. With an initial pressure of 231 mm a drop to only 187 mm is observed.

Methyl acetylene does not polymerize readily even at 475° at which temperature appreciable decomposition occurs. Isomerization to allene is negligible—not exceeding 1 percent which is within the errors of measurement.

Allene polymerizes measurably in the temperature range of 320–400°. The kinetics appear to be quite complex; rate constants calculated from point to point increase rapidly with time and

TABLE I. *Vinyl acetylene.*

| T °K | 533 | 533 | 533 | 577 | 577 | 577 | 613 | 613 | 613 |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| P_0 mm | 209.1 | 380.0 | 443.0 | 113.1 | 214.4 | 602.6 | 118.4 | 216.8 | 361.0 |
| $k_0 \times 10^6$ (% reaction) ⁻¹ sec. ⁻¹ | 0.335 | 0.512 | 1.17 | 0.159 | 0.257 | 1.16 | 0.301 | 1.24 | 1.89 |

TABLE II. *Vinyl acetylene—effect of O_2 ; 577°K.*

| P_0 MM | $k \times 10^6$ (AT 10% REACTION) (% REACTION) ⁻¹ SEC. ⁻¹ | |
|----------|--|---------------|
| 186.1 | 0.386 | no oxygen |
| 214.8 | 0.623 | 8.9 mm of air |

oxygen accelerates the reaction noticeably. No isomerization into methyl acetylene was found to take place. Several workers^{2d, 16} have shown that allene and its derivatives can be isomerized into corresponding acetylenes by means of an alkaline catalyst. In pyrolyzing allene and methyl acetylene, Hurd¹⁷ found the polymerization products of both in the pyrolysis of either and concluded that some isomerization was present. The pyrolyses were done between 400–600° with the flow method and a contact time of about one minute. Polymerization and decomposition were the predominant reactions.

The absence of the isomerization reaction is noteworthy as demonstrating that the direct shift of a hydrogen from one carbon atom to another requires a high activation energy, not less than 40,000 cal. if the A factor of its rate constant is of the order of 10^{13} . This observation is probably of quite general validity as suggested by other work in this laboratory on several hydrocarbons.

Vinylacetylene starts to polymerize appreciably at ca. 200°. The reaction was followed between

¹⁶ Slobodin, (a) J. Gen. Chem. (U.S.S.R.) 4, 778 (1934); (b) *ibid.* 5, 48 (1935).

¹⁷ Hurd and Meinert, J. Am. Chem. Soc. 52, 4540 (1930).

260–340° with no serious complications from decomposition occurring. However, the pressure drops to one-fourth or even less of the initial pressure, indicating that the reaction does not effectively stop at the dimer stage, as is the case with dienes, but proceeds with undiminished velocity to higher polymers. During a run the order is quite high and so is the dependence on the initial pressure, as shown in Tables I and II. The second order constants in these tables were calculated with percent of the total pressure drop as the measure of the instantaneous concentration of the reactant and extrapolated to initial time. The reaction appears to be reproducible but is accelerated by appreciable quantities of oxygen as indicated in Table II. The disentanglement of the kinetics of the primary reaction from those of the secondary ones would be a rather difficult task and the study of the reaction was abandoned.

In *cyclopentadiene* dimerization the equilibrium is so far on the side of the monomer that pressures near and above one atmosphere must be used to obtain a reasonable extent of the reaction. The decomposition, on the other hand, can be conveniently followed to practical completion at lower pressures. The second order of the association reaction, after correcting for the reverse process, is not well preserved during various runs as will be seen from Table III in which two typical runs have been reproduced. The trend of the constants varies with temperature. The initial constants, however, seem to be decidedly of the second order with respect to the pressure of the reactant, which is encouraging—particularly so because the decomposition reaction is of a good first order during the entire course of different runs as seen in Table IV.

Thus it is believed that drifts of the association rate constants are due to secondary reactions. It will be noted that the addition of a considerable quantity of oxygen does not influence the association reaction, which further lessens the chance for a chain mechanism in this case. Tables V and

TABLE III. *Dimerization of cyclopentadiene; gas phase.*

| Percent Reactant k cc mole ⁻¹ sec. ⁻¹ | I. 466.6°K $P_0 = 1450$ mm | | | | | | | | | | | |
|--|-----------------------------|------|------|------|------|------|------|------|------|--|--|--|
| | 96.8 | 91.2 | 85.8 | 80.7 | 75.0 | 70.9 | 67.7 | 64.4 | 62.0 | | | |
| | 10.2 | 10.5 | 11.0 | 12.2 | 13.3 | 14.3 | 15.8 | 16.9 | | | | |
| Percent Reactant k cc mole ⁻¹ sec. ⁻¹ | II. 426.1°K $P_0 = 1380$ mm | | | | | | | | | | | |
| | 98.7 | 96.2 | 92.5 | 87.3 | 82.3 | 76.3 | 69.7 | 64.2 | | | | |
| | 1.96 | 2.05 | 1.83 | 1.87 | 1.79 | 1.77 | 1.71 | | | | | |

VI give the summaries of the rate constants of the association and decomposition reactions. The former can be cast into the form: $k_{\text{assn}} = 8.5 \times 10^7 \exp(-14900/RT)$ cc mole⁻¹ sec.⁻¹ and the latter: $k_{\text{decomp}} = 1.0 \times 10^{13} \exp(-33700/RT)$ sec.⁻¹.

The dimerization of pure cyclopentadiene in the liquid phase has been studied by Stobbe and Reuss¹⁸ while quite recently Khambata and Wassermann¹⁹ have briefly reported their results on the rate of dimerization in benzene as a solvent and on the rate of decomposition of the dimer in paraffin oil. Our experiments were performed with pure cyclopentadiene and with cyclopentadiene in tetrahydronaphthalene. In dilute solutions and even in the 50-50 mixture with tetrahydronaphthalene the reaction was found to be of a good second order, but pure cyclopentadiene was found to polymerize in a nearly first-order reaction as noted in an earlier publication,²⁰ although the initial second-order constants agreed with those obtained in solution.

It was suggested in the preliminary note that this behavior might be of general significance for polymerizations in the condensed phase but in the meantime results have been obtained which definitely show that the anomaly is due to an incorrect estimation of the concentration of

TABLE IV. *Decomposition of dicyclopentadiene; gas phase. 472.4°K.*

| <i>P</i> mm <i>Δt</i> sec. <i>k</i> × 10 ³ sec. ⁻¹ | 37.6 | 41.4 91 | 45.6 117 | 48.5 95 | 54.8 285 | 58.5 274 | 60.9 292 | 62.5 396 | 64.1 1067 |
|--|------|------------|-------------|------------|-------------|-------------|-------------|-------------|--------------|
| | | 1.60 | 1.73 | 1.77 | 1.82 | 1.77 | 1.85 | 1.60 | 1.93 |

TABLE V. *Association of cyclopentadiene; gas phase.*

| <i>T</i> °K | <i>P</i> ₀ MM | <i>k</i> CC MOLE ⁻¹ SEC. ⁻¹ | <i>T</i> °K | <i>P</i> ₀ MM | <i>k</i> CC MOLE ⁻¹ SEC. ⁻¹ |
|-------------|--------------------------|--|-------------|--------------------------|--|
| 393.4 | 1600 | 0.467 | 433.9 | 1442 | 2.32 |
| 394.6 | 1052 | .438 | 433.4 | 1100 | 2.32 |
| 394.6 | 1880 | .448 | 432.5 | 1100 | 2.74 |
| 394.6 | 1835 | .493† | 432.5 | 680 | 2.60 |
| 400.2 | 1217 | .505* | 451.1 | 833 | 4.78‡ |
| 413.1 | 977 | 1.04 | 451.1 | 1240 | 4.78‡ |
| 412.6 | 1880 | 1.02 | 452.1 | 529 | 4.65‡ |
| 412.1 | 1066 | 1.39 | 452.1 | 629 | 4.37‡ |
| 411.9 | 777 | 1.03 | 453.1 | 442 | 4.93‡ |
| 426.1 | 1380 | 1.88 | 453.1 | 709 | 4.06‡ |
| 432.3 | 1229 | 2.48 | 450.1 | 526 | 4.65‡ |
| 432.9 | 373 | 2.56 | 463.1 | 1230 | 8.07 |
| 433.1 | 896 | 2.48 | 465.3 | 1340 | 8.37 |
| 433.1 | 678 | 2.54 | 466.6 | 1450 | 9.56 |

¹⁸ Stobbe and Reuss, Ann. **391**, 151 (1912).

¹⁹ Khambata and Wassermann, Nature **137**, 496 (1936).

²⁰ Kistiakowsky and Mears, J. Am. Chem. Soc. **58**, 1060 (1936).

TABLE VI. *Decomposition of dicyclopentadiene; gas phase.*

| <i>T</i> °K | <i>P</i> ₀ MM | <i>k</i> × 10 ³ SEC. ⁻¹ | <i>T</i> °K | <i>P</i> ₀ MM | <i>k</i> × 10 ³ SEC. ⁻¹ |
|-------------|--------------------------|--|-------------|--------------------------|--|
| 428.0 | 157.4 | 0.060 | 473.1 | 16.8 | 1.57 |
| 428.4 | 155.3 | .070 | 480.1 | 197.2 | 3.74 |
| 429.6 | 178.7 | .080 | 483.1 | 145.1 | 3.58 |
| 455.6 | 145.1 | .53 | 493.9 | 19.8 | 9.24 |
| 456.6 | 60.3 | .49 | 494.0 | 93.5 | 9.13 |
| 469.1 | 116.9 | 1.17* | 494.1 | 31.1 | 8.54 |
| 472.4 | 37.6 | 1.75 | 494.1 | 83.5 | 9.32 |
| 472.9 | 106.0 | 1.93 | 494.5 | 32.4 | 9.52 |
| | | | 495.4 | 45.4 | 9.15 |

* Packed flask.

† Addition of 22 mm air.

‡ These data, because of experimental imperfections, are given less weight than the experiments at 465°.

TABLE VII.

Assn. of Pure Cyclopentadiene 312.7°K Assn. of Cyclopentadiene in Dimer 344.3°K

| <i>t</i> SEC. | CONC. MOLE/CC | <i>k</i> × 10 ³ CC MOLE ⁻¹ SEC. ⁻¹ | <i>k</i> * × 10 ³ CC MOLE ⁻¹ SEC. ⁻¹ | <i>t</i> SEC. | CONC. MOLE/CC | <i>k</i> × 10 ² CC MOLE ⁻¹ SEC. ⁻¹ |
|---------------|------------------|---|---|---------------|------------------|---|
| 0 | 0.0118 | | | 0 | 0.0027 | |
| 3180 | .0108 | 2.63 | 2.92 | 1200 | .0022 | 5.94 |
| 7200 | .0093 | 3.70 | 3.55 | 4740 | .0015 | 6.22 |
| 11460 | .0083 | 3.83 | 2.99 | 12360 | .0010 | 4.14 |
| 26260 | .0057 | 3.92 | 2.20 | 16380 | .0008 | 5.29 |
| 69240 | .0023 | 5.83 | 2.82 | | | |
| | | | | 0 | .0027 | |
| | | | | 20160 | .0007 | 5.20 |

* Corrected for formation of polymer on the basis of experiments by Terent'eff and Solochin²¹ and of Stobbe and Reuss.¹⁸

cyclopentadiene during the latter stages of the reaction. In Table VII are given the results of a run in which pure cyclopentadiene was used as the starting substance and low concentrations of the reactant were obtained by prolonged heating. In the other runs presented the initial substance was a mixture of a small amount of monomer, the rest being dimer, which mixture was made by weighing and was used as reference in interferometer readings. The figures in the table show quite clearly that the dilute mixture gives a good second-order constant instead of following the trend established in the run with pure monomer.

The explanation of this behavior is found in a paper by Terent'eff and Solochin²¹ who found that a polymer is formed in pure liquid cyclopentadiene in addition to the dimer. According to their data this reaction occurs chiefly in the beginning of the main process and hence the monomer, rather than the dimer, is responsible for the polymer formation. The refractive index of the mixture of monomer, dimer and polymer is

²¹ Terent'eff and Solochin, Sintet. Kauchuk **5**, 9 (1933).

TABLE VIII. Dimerization of pure liquid cyclopentadiene. Rate constants from extrapolation to zero time.

| T °K | k_0 CC MOLE ⁻¹ SEC. ⁻¹ |
|-------|---|
| 273.1 | 4.50×10^{-5} |
| 313.0 | 2.82×10^{-3} |
| 317.9 | 3.50×10^{-3} |
| 331.3 | 1.30×10^{-2} |
| 333.1 | 1.05×10^{-2} |
| 353.1 | 4.63×10^{-2} |
| 354.1 | 4.50×10^{-2} |
| 354.3 | 6.00×10^{-2} |
| 344.3 | 5.26×10^{-2} (in dimer solution) |
| 344.3 | 2.80×10^{-2} (interpolated for pure monomer) |
| 344.3 | 4.14×10^{-2} (tetrahydronaphthalene solutions) |

TABLE IX. Association of cyclopentadiene in tetrahydronaphthalene.

| T °K | CONC. MOLE/CC | k CC MOLE ⁻¹ SEC. ⁻¹ |
|-------|-----------------------|---|
| 344.3 | 0.39×10^{-3} | 4.82×10^{-2} |
| 344.3 | 1.28 | 3.99 |
| 344.3 | 1.28 | 4.18 |
| 318.1 | 6.44 | 0.538 |
| 318.1 | 6.44 | .516 |
| 318.1 | 1.40 | .556 |

different from a mixture containing only the dimer and the same amount of monomer, such as those used for the calibration of the refractometer²² and hence an error is committed in following the course of the reaction by the refractometer. The percentage error in determining the concentration of the monomer increases rapidly towards the end of the reaction, the amount found being smaller than that actually present. Hence the rising second-order constants. Of course, because of the method of preparation, the correct concentration of the monomer was known in those runs in which prepared monomer-dimer mixtures were used by us and hence these runs gave results agreeing essentially with the initial constants of the others. The second-order constants of the pure monomer runs were extrapolated to initial time (see Table VIII) and the resulting k_0 's, when plotted logarithmically against inverse temperature, gave a reasonably straight line. The rate constant is found to be: $k = 2.0 \times 10^9 \exp(-17100/RT)$ cc mole⁻¹ sec.⁻¹.

Table IX gives the results of polymerization runs in tetrahydronaphthalene as solvent. It was unnecessary to extrapolate to initial time because the second order held quite well in these runs,

²² Dimer was freshly distilled to free it from polymer for this purpose.

except in the 50 wt. percent mixtures which showed a slight rise in their second-order constants—doubtless attributable to the occurrence of a slight polymerization to high molecular weight compounds.

Taking the averages of the rate constants at the two temperatures and evaluating from them the activation energy, the rate constant is cast into the form: $k = 4.2 \times 10^9 \exp(-17300/RT)$ cc mole⁻¹ sec.⁻¹. This expression agrees, as well as can be expected, with the data obtained with solutions of monomer in dimer. There is, however, a larger discrepancy with the results in pure monomer, as will be seen by inspecting the bottom of Table VIII. It is believed that the latter data are at fault because only at lower temperatures was the correction by the method of Terentief and Solochin successful in producing a second order rate. At higher temperatures, even after correction, the second order constants showed a tendency to increase during a run. One must conclude that here the polymerization is more pronounced (compare data on gas phase association for similar tendencies) and that altogether the extrapolation to initial time gives only the order of magnitude of the rate constant.

The results of the present studies on liquid phase polymerization agree with other available data. Thus, Stobbe and Reuss¹⁸ got for 20°: $k = 3.3 \times 10^{-4}$ cc mole⁻¹ sec.⁻¹ (as calculated by us) whereas the previously given expression yields for 20°: $k = 3.1 \times 10^{-4}$ cc mole⁻¹ sec.⁻¹. Khambata and Wassermann¹⁹ select for their data in benzene solution the representation: $k = 1.2$

TABLE X.

| Δt SEC. | 1,3-PENTADIENE | 652.9°K k CC MOLE ⁻¹ SEC. ⁻¹ |
|--------------------|----------------|--|
| | P, MM | |
| 0 | 315.0 | |
| 285 | 294.0 | 70.4 |
| 180 | 283.7 | 67.5 |
| 235 | 273.1 | 63.0 |
| 245 | 264.1 | 60.6 |
| 390 | 252.7 | 58.6 |
| 380 | 244.1 | 55.8 |
| 630 | 233.6 | 51.7 |
| 1315 | 220.9 | 40.2 |

$\times 10^9 \exp(-16400/RT)$ cc mole⁻¹ sec.⁻¹; for 71°C this gives: $k = 4.6 \times 10^{-2}$ and we find for tetrahydronaphthalene solution: $k = 4.3 \times 10^{-2}$. Notwithstanding considerable difference in the

form of the expression, gas phase data also lead to nearly the same rates. By extrapolation to 71°, $k = 3.1 \times 10^{-2}$ cc mole⁻¹ sec.⁻¹. The present data on the dissociation of dicyclopentadiene in the

TABLE XI.

| 2,3-DIMETHYL BUTADIENE-1,3 | | 652.6°K |
|----------------------------|-------|---|
| Δt SEC. | P, MM | k CC MOLE ⁻¹ SEC. ⁻¹ |
| 0 | 194.8 | |
| 180 | 191.1 | 46.0 |
| 540 | 181.6 | 45.6 |
| 180 | 178.8 | 46.0 |
| 600 | 170.7 | 46.0 |
| 600 | 165.2 | 37.8 |
| 300 | 163.4 | 27.2 |
| 660 | 160.8 | 19.1 |
| 540 | 159.8 | 9.4 |

gas phase and those of Khambata and Wassermann on the reaction in paraffin oil, $k = 6 \times 10^{12}$ exp $(-34000/RT)$ sec.⁻¹, while superficially similar, give quite different rates; thus at 500°K the gas rate is 2.5 times faster, so that in the liquid the equilibrium is shifted to the side of the dimer.

1,3-Pentadiene and 2,3-dimethyl butadiene-1,3 polymerize to dimers at measurable rates not unduly complicated by side reactions. Tables X and XI show the order of reaction during typical runs, while Tables XII and XIII are summaries of all the constants obtained.

The second order is seen to be reasonably well preserved during the initial stages of the reactions. At later times the constants fall off. The explanation of this behavior is to be found in decomposition (either of the reactants or the reaction products) accompanied by an increase in pressure, in complete analogy with the observations of Vaughan^{7b} on isoprene. The side reactions are relatively more pronounced at higher temperatures. Thus, in the case of 1,3-pentadiene, at 279° an initial pressure of 265 mm decreased to 162 mm (61 percent of the initial) but at 380° the pressure decrease was from 315 mm to 214 mm (68 percent). With 2,3-dimethyl butadiene-1,3 at 307.5°, the final pressure was 64.2 percent of the initial (290 mm to 186 mm) while at 352° the pressure dropped from 264 mm to only 206 mm (78 percent).

In addition to the decomposition, some formation of higher polymers also goes on, as evidenced by the presence of practically nonvolatile prod-

ucts. Thus, the interpretation of the latter stages of the reaction is rather uncertain and even in the beginning one is not justified in ascribing the entire pressure change to the formation of the dimers. However, because of the difficulty of more exact identification of the course of these reactions, it has been assumed here that in the beginning the entire pressure change is due to the dimer formation. It is to be noted that Vaughan^{7a} found with 1,3-butadiene that the second order constants increased during his runs. Hence, the decomposition is less important in this case than the formation of polymers, which is contrary to what has been observed for the other dienes.

With 2,3-dimethyl butadiene-1,3²³ an additional difficulty was encountered in that the three samples tried gave discordant results. The rates obtained with sample I were 17 percent and 43 percent faster than those found with samples II and III, respectively. However, the temperature coefficients are identical within experimental errors. Furthermore, each sample gave self-consistent results and the rates appeared to be uninfluenced by traces of oxygen. In view of this we are inclined to interpret the discrepancy as being due to a greater purity of sample I. If

TABLE XII. 1,3-Pentadiene.

| °K | k CC MOLE ⁻¹ SEC. ⁻¹ | °K | k CC MOLE ⁻¹ SEC. ⁻¹ |
|-------|---|-------|---|
| 552.1 | 1.85 | 652.9 | 67.8 |
| 552.1 | 1.86 | 652.9 | 66.8 |
| 616.6 | 22.4 | 652.9 | 64.7 |
| 616.6 | 22.5 | 668.9 | 109.3 |
| 651.8 | 68.3 | 692.1 | 221.0 |

TABLE XIII. 2,3-Dimethyl butadiene-1,3.

| SAMPLE I | | SAMPLE II | | SAMPLE III | |
|----------|---|-----------|---|------------|---|
| °K | k cc mole ⁻¹ sec. ⁻¹ | °K | k cc mole ⁻¹ sec. ⁻¹ | °K | k cc mole ⁻¹ sec. ⁻¹ |
| 582.1 | 4.4 | 626.8 | 18.3 | 610.6 | 10.0 |
| 652.6 | 46.0 | 626.8 | 18.3 | 611.4 | 9.5 |
| 653.6 | 50.8 | 653.1 | 39.4 | 655.5 | 33.8 |
| 653.6 | 44.6 | 654.3 | 43.0 | 655.8 | 36.0 |
| 654.1 | 49.9 | 668.6 | 59.1 | 655.8 | 35.7 |
| 668.6 | 69.1 | 668.6 | 69.3 | 670.3 | 54.8 |
| 673.1 | 96.7 | 672.1 | 70.1 | 670.3 | 57.6 |
| | | | | 670.3 | 53.9 |
| | | | | 671.1 | 53.5 |

²³ Samples of 2,3-dimethyl butadiene-1,3 that were sealed in absence of air and kept indefinitely at room temperatures polymerized into solid, white masses.

sample I is assumed to be 100 percent pure, sample II must contain *ca.* 8 percent and sample III *ca.* 17 percent of nonpolymerizable impurities. It is to be noted in this connection that Kistiakowsky and Lacher⁹ reported slightly higher rates with 1,3-butadiene and isoprene than those given by Vaughan.⁷ Since the latter used compounds of an ordinary degree of purity, as contrasted with highly purified samples of the former, it was also concluded that impurities accounted for the discordant results. In view of the difficulty of purifying these compounds, such an explanation seems to us to be entirely reasonable, but the *A* factors of all the rate constants must be regarded as uncertain perhaps to the extent of 20 percent. Since the uncertainty arising from errors in the determination of the activation energies is many times greater, this added error is not very serious.

The activation energy of the 2,3-dimethyl butadiene-1,3 polymerization is found to be 25,300 cal.; $k = 1.45 \times 10^{10} \exp (-25300/RT)$ cc mole⁻¹ sec.⁻¹.

A similar plot of the data from Table XII leads to an activation energy of 26,000 cal. for 1,3-pentadiene and $k = 3.5 \times 10^{10} \exp (-26000/RT)$ cc mole⁻¹ sec.⁻¹.

The literature contains several reports on the structure of the dimers formed in polymerization of the dienes. Lebedev² identified the product of the dimerization of 1,3-butadiene as 1-vinyl cyclohexene-3 and later studies by many workers^{2, 3, 24-31} showed that the homologs of 1,3-butadiene also underwent simultaneous 1,4- and 1,2-addition, thereby making this reaction completely analogous to the Diels-Alder condensation.³²⁻³⁵ The compounds analyzed were obtained by heating sealed tubes filled with

dienes and hence were formed at high pressures of the vapor or even in liquid phase reactions. Vaughan^{7a} reported, on the other hand, a dicyclic compound as the dimerization product of 1,3-butadiene at higher temperatures and low pressures. However, his very small samples were collected at the ends of runs and were allowed to stand exposed to air for varying lengths of time. It seemed advisable, therefore, to redetermine the structure of this dimer. 1,3-Butadiene vapor was heated at pressures below atmospheric and at temperatures close to 370° in a 12-liter flask for sufficient lengths of time to produce *ca.* 50 percent conversion according to the data of Vaughan. Combined products from several runs were subjected to fractionation in a three-foot Podbielniak-type column. The main fraction (but by no means all—considerable quantities of higher boiling material remained in the pot) boiled at $129.4 \pm 0.5^\circ$ at 760 mm; refractive index, $n_D^{20} = 1.4637$; density = 0.8237 at 25°. The molecular refraction, therefore, is 36.16 whereas the theoretical molecular refraction³⁶ for the product of 1,4- and 1,2-addition is 36.22. A portion of the dimerization product was hydrogenated by the Adams catalyst at room temperature without a solvent.³⁷ The sample took up 1.68 mole of hydrogen per mole of sample and the physical constants of the product were: b.p. 131.2° at 760 mm; $n_D^{20} = 1.4333$ and $d_{25}^{20} = 0.7811$, which constants agree closely with those of ethyl cyclohexane. Another portion of the product was brominated at -5° and twice recrystallized from alcohol. M.p. = $69-71^\circ$ which agrees with the melting point of 3,4,1¹,1²-tetrabrom-1-ethyl cyclohexane. In view of all these data, no doubts can remain that in the high temperature, low pressure reaction the addition goes via the same chemical mechanism as the dimerization at lower temperatures and high concentrations.³⁸ Similar tests were not performed on other open chain dienes herein investigated but little doubt can exist that their products are also cyclohexene derivatives.

²⁴ Richard, *Comptes rendus* **153**, 116 (1911).

²⁵ Kogerman, *Naturforscher Ges.* **41**, Nr. 3/4, 59 (1934).

²⁶ Slobodin, *J. Gen. Chem. (U.S.S.R.)* **5**, 1415 (1935).

²⁷ Harries, *Ann.* **383**, 157 (1911).

²⁸ Aschan and Krohn, (a) *Ber.* **57B**, 1959 (1924); (b) *Ann.* **439**, 221 (1924).

²⁹ Tilden, *J. Chem. Soc.* **45**, 410 (1884).

³⁰ Wallach, *Ann.* **227**, 295 (1885); *J. Chem. Soc.* **48**, 550 (1885).

³¹ Ostromislensky and Koschelev, *J. Russ. Phys. Chem. Soc.* **47**, 1928 (1915); *J. Soc. Chem. Ind.* **35**, 368 (1916).

³² Diels and Alder, (a) *Ann.* **460**, 119 (1928); (b) *ibid.* **470**, 68 (1929).

³³ Alder, *Handbuch der biologischen Arbeitsmethoden*, ed. Abderhalden, Teil 2, 2 Hälfte, Heft 9 (1933).

³⁴ Kohler and Kable, *J. Am. Chem. Soc.* **57**, 917 (1935).

³⁵ Littmann, *ibid.* **58**, 1316 (1936).

³⁶ Getman and Daniels, *Outlines of Theoretical Chemistry*, fifth edition (J. Wiley and Sons, Inc., New York, 1931), p. 93.

³⁷ The low pressure hydrogenation outfit and the catalyst were the property of Dr. E. B. Hershberg of this laboratory who kindly placed them at our disposal.

³⁸ Cf. also Woljinski, Jegis, Rubin and Shereuretieff, *Sintet. Kauchuk* **5**, 8 (1936), who arrive at the same conclusion.

TABLE XIV.

| ASSOCIATIONS | RATE CONSTANT CC MOLE ⁻¹ SEC. ⁻¹ | REF. |
|--|--|------|
| 2 1,3-Butadiene | $4.7 \times 10^{10} \exp(-25300/RT)$ | 7a |
| 2 Isoprene | $5.3 \times 10^{11} \exp(-28900/RT)$ ($4.7 \times 10^{10} \exp(-25900/RT)$) | 7b |
| 2 1,3-Pentadiene | $3.5 \times 10^{10} \exp(-26000/RT)$ | |
| 2 2,3-Dimethyl butadiene-1,3 | $1.45 \times 10^{10} \exp(-25300/RT)$ | |
| 2 Cyclopentadiene | $8.5 \times 10^7 \exp(-14900/RT)$ | |
| 1,3-Butadiene and acrolein | $1.46 \times 10^9 \exp(-19700/RT)$ | 9 |
| Isoprene and acrolein | $1.02 \times 10^9 \exp(-18700/RT)$ | 9 |
| 1,3-Butadiene and crotonic aldehyde | $0.90 \times 10^9 \exp(-22000/RT)$ | 9 |
| Cyclopentadiene and acrolein | $1.02 \times 10^9 \exp(-15200/RT)$ | 9 |
| <i>Decompositions</i> | | |
| Endomethylene-2,5-tetrahydrobenzaldehyde | $2.2 \times 10^{12} \exp(-33600/RT) \text{ sec.}^{-1}$ | 9 |
| Dicyclopentadiene | $1.0 \times 10^{13} \exp(-33700/RT) \text{ sec.}^{-1}$ | |

The product of the dimerization of cyclopentadiene has been discussed in the literature and its structure identified as that resulting from 1,4- and 1,2-addition. According to Alder and Stein,³⁹ the dimer exists in two forms, α and β , which can be respectively described as the "chair" and the "trough" of the tricyclic compound. The second predominates at temperatures below 170° and it is reasonable to think that in the present research this form was the main product, although some divergence between the results of the gas phase experiments, performed at higher average temperatures, and those in the liquid phase can be tentatively ascribed to the formation of the two different forms.

INTERPRETATION OF THE RESULTS

Results obtained in this and in earlier work on the rates of 1,4- and 1,2-addition reactions of the dienes are now sufficiently numerous to permit an attempt at a more comprehensive treatment of their kinetics. In Table XIV all the pertinent data have been summarized. The association reactions can be divided into three main groups according to the magnitude of their temperature-independent factors. The four 1,3-butadiene polymerizations have, within experimental error, identical A factors. Isoprene constitutes the only appreciable deviation but this reaction according to Vaughan is not very clean. Furthermore, its activation energy falls entirely out of line with those of its homologs, both the less and the more complex ones. When the absolute rates are computed, isoprene is found to have a rate falling between those of 1,3-butadiene and 1,3-penta-

diene.⁴⁰ Hence the abnormality of the A factor of isoprene may be attributed to experimental imperfections and the rate expression considered to be approximately that given in brackets. It is, however, rather difficult to believe that the temperature independent constants of all these four reactions should be reduced by a further average factor of thirty—or those of the four Diels-Alder condensations increased by the same factor—to make the constants of all eight reactions identical. A careful study of all plausible systematic errors fails to reveal any justification for such a change⁴¹ and we must consider, provisionally at least, the A factors in the two groups as being distinctly different. Also, the polymerization of cyclopentadiene can hardly be brought into agreement with the others. In order to do so one must alter rate constants at the extreme ends of the temperature range covered by nearly 50 percent.⁴² If the gaseous rate ex-

⁴⁰ Thus, at 350° the rate constants of these four reactions, in their order as in Table XIV, are: 63, 38, 26 and 19.5 cc mole⁻¹ sec.⁻¹. It is to be noted that the variations are quite small and in no way confirm the statement of Gapon (reference 3b) that the introduction of each methyl group into 1,3-butadiene decreases the rate by a factor of six.

⁴¹ Particularly convincing evidence against systematic errors is that the drifts of rate constants during the course of a run in these eight reactions are in no way correlated to the magnitude of their A factors.

⁴² The A factors of the other reactions are on the whole more reliably determined but individual variations of almost a factor of ten are not excluded. Quite recently Khambata and Wassermann, in a short note (Nature **139**, 669 (1937)), report the gaseous association rate of cyclopentadiene to be given by $1.3 \times 10^9 \exp(-16700/RT)$ cc mole⁻¹ sec.⁻¹. The temperature range covered in their experiments is smaller than ours. Since this expression agrees more closely with that of the liquid phase reaction, it is inherently more probable. The difference may well be within the combined experimental errors and in the absence of more detailed information it is impossible for us to evaluate critically the relative merits of the two sets of experiments.

³⁹ Alder and Stein, Ann. **504**, 219 (1933).

pression is correct, the change of the A factor of this association reaction in going from the gas phase to solutions forms an interesting example of the effect of liquid state of aggregation on the form of rate expressions.

Both decompositions are fairly clean-cut reactions and on this score no particular objections to the rate data can be raised. However, the temperature ranges covered are small and particularly in the case of endomethylene-2,5-tetrahydrobenzaldehyde a considerable error in the activation energy is not excluded since the instantaneous concentrations of the reactant could only be estimated from the total pressure changes in the reaction and were quite low in practically all of the experiments.

In an earlier paper Kistiakowsky and Lacher⁹ have discussed the statistical calculation of the temperature independent factor assuming that the intermediate complex has a structure very similar to that of the final addition product. Their conclusion was that, while the agreement was not too good, the statistical treatment on this basis did give reasonable results. The real situation, however, is more involved than they have inferred. Since the A factor of the decomposition reaction of endomethylene-2,5-tetrahydrobenzaldehyde has a magnitude of slightly less than kT/h , the activated complex cannot be more loosely bound together than the associated molecule. Therefore, this latter, just as the activated complex itself, must contain six frequencies of a magnitude of $100\text{--}150\text{ cm}^{-1}$ and these do not include torsional and other vibrations of the side chains because in the treatment of association reactions to the first approximation they cancel against the corresponding vibrations of the monomer reactant molecules. The situation is still less satisfactory for the associations of 1,3-butadiene and its homologs, as even lower frequencies must be assumed for the ring because of their larger A factors. While no complete analysis of the vibrational frequencies of cyclohexene is available, the existent data⁴³ strongly discourage this assumption.

Thermodynamic considerations also show that something must be wrong with the data; namely, the entropy change in the Diels-Alder condensa-

tion of acrolein and cyclopentadiene, as calculated from kinetic data, is impossibly small: 37 E.U. (at 1 atmos.). It is of the order of magnitude of the entropy change in additions of halogen hydrides to isobutene⁴⁴ and is actually a little smaller than the entropy change in typical polymerizations of two mono-olefins to another mono-olefin such as the condensation of two molecules of propylene to one of n -hexylene.⁴⁵ In the former of these reactions one of the reactants is a diatomic molecule and in both processes the reaction does not lead to a stiffening of the molecular structure as it does in diene polymerizations. Hence, a much greater entropy decrease is to be expected for this latter type of reaction. The newly added cyclopentadiene polymerization does show the expected entropy change (50 E.U.) and a simple comparison with this reaction would suggest that the error lies in the A factors of the other eight association reactions. However, this seems to us most unlikely. The reactions have been studied by three investigators, using independently calibrated temperature and pressure measuring devices and techniques which were different in many details. We are confident that the error must lie with the rate constant of the only known decomposition reaction of this group—that of endomethylene-2,5-tetrahydrobenzaldehyde. Instead of the measured value of $2 \times 10^{12}\text{ sec}^{-1}$, the A factor for this reaction must be of the order of 10^{16} which would bring the entropy change for this reaction into line with those of others.

The numerically large A factors of both forward and reverse rates of the association reactions are to be interpreted statistically as meaning, in the terminology of Eyring,⁴⁶ that the activated complex has a very loose structure. This requirement is met if the activated complex is supposed to have essentially the configuration of a free radical. But other evidence, to be considered presently, suggests that free radicals may have a more real existence than that of activated complexes and hence the detailed reaction mechanism should involve the association of two molecules,

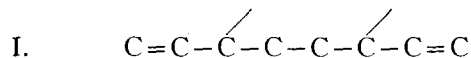
⁴⁴ Kistiakowsky and Stauffer, *J. Am. Chem. Soc.* **59**, 165 (1937).

⁴⁵ Parks and Huffman, *Free Energy Changes of Organic Compounds* (Chemical Catalog Co., New York, 1932), p. 81.

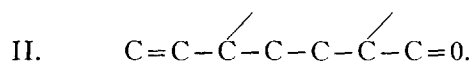
⁴⁶ Eyring, *J. Chem. Phys.* **3**, 107 (1935).

⁴³ Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931).

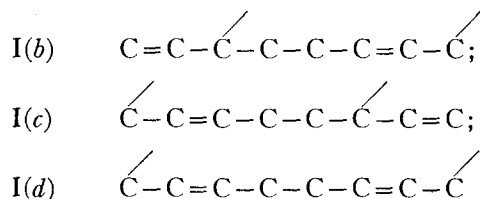
via an activated complex, to a free radical, which then may, through another active configuration, form the ring structure characteristic of the final product. The concept of free radical intermediates in polymerizations of unsaturated compounds is not new but to conserve space the pertinent literature will not be reviewed. The free radical in the case of 1,3-butadiene must have the structure:



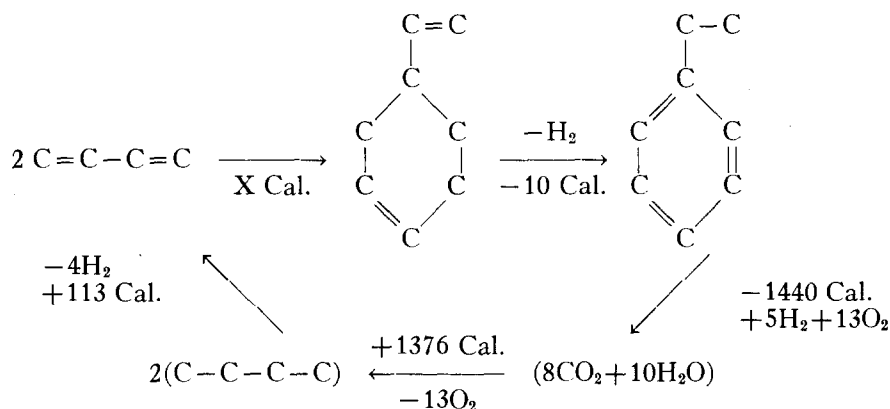
or, in the simplest Diels-Alder condensation:



The first question is whether enough energy is available to form such radicals. With activation energies of the order of only 15,000–25,000 cal. it might seem most unlikely, but it should be remembered that radicals of this type can be stabilized by resonance. It is readily seen that four energetically equivalent electronic structures are possible for both molecules I and II:



Dr. J. B. Howard of this laboratory has kindly calculated for us by the method of Pauling⁴⁷ the magnitude of this resonance energy using for the unknown exchange integral the value deduced by Pauling from his interpretation of benzene resonance. The energy which Dr. Howard finds, 1.4 ev (32.2 Cal.), is undoubtedly too large as are practically all of the resonance energies thus calculated. If it is multiplied by a factor of 0.5, which brings calculation and experiment into fair agreement in many other cases,¹⁴ a value of some 15–20 Cal. results which may be regarded as substantially correct. Together with the activation energy of the association reactions, there are thus some 35–50 Cal. available to form the radical. To connect this figure with the more familiar thermochemical data, consider the following cycle:



in which all steps, except the heat of combustion of ethyl benzene,⁴⁸ have been taken from Rossini's data⁴⁹ or calculated from the heats of hydrogenation^{14, 50} so that the result, $X = -39$ Cal., is fairly reliable.

The reaction in which 39 Cal. are given off involves the breaking of two double bonds to

single ones and the formation of two single bonds. Hence, the difference of energy requirements of

the processes: $\text{C}=\text{C} \rightarrow \text{C}-\text{C}$ and $\text{C}-\text{C} \rightarrow \text{C}+\text{C}$ is 19.5 Cal. or, correcting for *ca.* 3 Cal. resonance energy in 1,3-butadiene, is approximately 22.5 Cal.⁵¹ The process of formation of the intermediate free radical involves the breaking of two

⁴⁷ Pauling and Sherman, J. Chem. Phys. 1, 362, 606, 679 (1933).

⁴⁸ Kharasch, Nat. Bur. Stand. J. Research 2, 359 (1929).

⁴⁹ Rossini, *ibid.* 12, 735 (1934).

⁵⁰ Dolliver, Gresham, Kistiakowsky and Vaughan, J. Am. Chem. Soc. 59, 831 (1937).

⁵¹ Compare this value with 20.5 cal. for the difference in heats of reaction between *n*-hexylene plus hydrogen to give *n*-hexane and *n*-hexane plus hydrogen to give two molecules of propane (reference 48).

double bonds (to single ones) and the formation of a new single bond. To allow this reaction, the following condition must be satisfied:

Energy of opening two double bonds to two single bonds + resonance in two 1,3-butadienes —energy of breaking a single bond—resonance in the radical < 25 Cal., the activation energy.

Combining this with the above figure, we find that, for free radicals to be formed, the energy of the single carbon-carbon bond must be not greater than 78 Cal., while the energy of opening a double bond must not be greater than 56 Cal. These figures are of a sensible magnitude, similar to those suggested in many recent publications on the kinetics of organic reactions; they cannot be materially raised without sacrificing the kinetic explanation of the decompositions of organic iodides by the catalysis of iodine atoms for which abundant evidence is available.⁵² The conclusion is that the thermal data now available do not exclude the formation of the free radicals.

There is considerable evidence, into the discussion of which we will not enter because of space considerations, that the dimer with the ring structure once formed does not undergo further polymerization. To account for the formation of open-chain polymers in conjunction with the dimer,⁵³ one must therefore suppose that two quite independent reactions occur simultaneously which have nearly identical activation energies,^{2d} because dimers and polymers are formed in commensurate yields over very wide temperature ranges in a given reaction. This is quite unnecessary if the free radicals are supposed to be formed and to have a life long enough that they may undergo further addition reactions—perhaps involving small activation energies. This process will preponderate under conditions of high concentration, whereas at low pressures of

the gases the main reaction is the rearrangement of the radical into the stable six-membered ring structure. If the primary reaction is the same for the formation of both the polymer and the dimer, the increase in the amount of the former with increasing concentration of the reactants must occur at the expense of the latter, whereas if the two reactions are independent, such a relation should not be found. This seems to be suitable for an experimental test and experiments in this direction are now in progress in this laboratory.

The observation of Diels and Alder^{52a} that transient color accompanies rapid diene synthesis, which has been quoted by Littmann³⁵ in support of the radical theory, is undoubtedly favorable, but so far color has been observed only in reactions involving quite complex molecules and other explanations are possible.

The intermediary free radical may also be used to explain the action of oxygen in accelerating polymerization at low temperatures by supposing that the oxygen is attached to one of the free valencies in a peroxide-like structure thereby preventing closure of the ring and encouraging further polymerization. This may occur in the instant of the primary reaction, making its activation energy and *A* factor quite different from those here described, or follow it after formation of the dimer radical. That the oxygen has no effect on these association reactions at high temperatures (see Vaughan, reference 7a) should be interpreted as meaning that now the peroxide has become too unstable to determine the kinetic course of the reaction.⁵⁴

We now turn to kinetic data which may be adduced to support the radical mechanism. A comparison of the activation energies of the nine association reactions involved is not decisive, but the evidence offered by the *A* factors is much more convincing. It has been pointed out before that the assumption of ring structure for the activated complex leads to impossibly low frequencies of the dimer molecule. If the activated complex has the structure of a free radical, this difficulty disappears because now some of the

⁵² Ogg, *Trans. Faraday Soc.* **31**, 482, 1385 (1935); *J. Am. Chem. Soc.* **56**, 526 (1934); *ibid.* **58**, 607 (1936). In the last paper Ogg interprets the mechanism of the decomposition of ethylene diiodide, studied by Arnold and Kistiakowsky, *J. Chem. Phys.* **1**, 166 (1933), in a way which suggests that the opening of a double bond requires only 25 Cal. This leads to highly improbable consequences and we must decline his interpretation of the reaction and retain instead the mechanism developed originally by Arnold and Kistiakowsky.

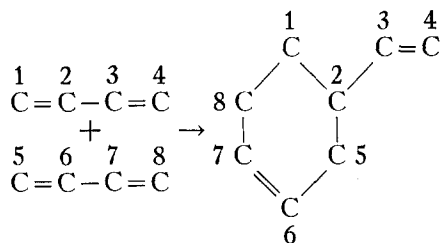
⁵³ Littmann (reference 35) has recently shown that, when polymers are formed in the Diels-Alder reaction in very concentrated mixtures, they contain both reactants in the molecule rather than the diene hydrocarbon alone.

⁵⁴ A situation analogous to this exists in the chlorine-carbon monoxide reaction where inhibition by oxygen, presumably due to the formation of ClO₂, ceases at higher temperatures because of the greater instability of this compound.

newly formed internal degrees of freedom are either free rotations or very slow torsional oscillations of an open chain around carbon-carbon single bonds.

Since the numerical values of the partition functions of such modes of motion are greater than those of vibration of a reasonable frequency, an increase of the calculated rate constant must result. Without going into detailed calculations, the value of which is minimized by the many inherent uncertainties, the following considerations will clarify the point. Evaluating Eyring's expression for a bimolecular rate constant in which only translational (6 for the reactants, 4 for the complex) and external rotational (6 for the reactants, 3 for the complex) degrees of freedom have been included, Pauling's values for internuclear distances being used throughout, one finds a value of $ca. 10^5 \exp(-E'/RT)$ with insignificant variations from one reaction to another in the group considered. The activation energy E' is at the "experimental" temperature but again only the external degrees of freedom have been included in the correction from absolute zero. The experimental A factors are some 10^3 to 10^5 times larger than the above value. These factors must be interpreted by considering the remaining internal degrees of freedom of which the product has more than the reactants.

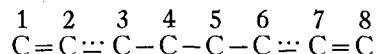
In the cyclic activated complex, as seen in the following diagram, there is one internal free rotation (2-3) against two (2-3, 6-7) in the reactant molecules:



The complex has six more vibrations than the two reactant molecules together. Hence, in the first approximation,⁵⁵ the ratio of the product of six vibrational partition functions to one internal rotation function must have values up to 10^5 —

whence the low frequencies calculated by Kistiakowsky and Lacher.⁹

In the case of the free radical intermediate:



the complex has three internal rotations, around bonds 3-4, 4-5, and 5-6. Probably no rotations are possible around the other bonds because of resonance. The complex has four more vibrations than the two reactants together and the additional factor in the rate expression, in the first approximation, equals the product of four vibrational functions times an internal rotation partition function. This latter is numerically equal to 25-100 for the different molecules here considered and hence only a relatively small residual factor needs to be assigned to the vibrational partition functions. Furthermore, since the structure of the complex is that of an open chain, lower frequencies of vibration are to be expected and so the difficulty disappears altogether.

While the explanation here offered is satisfactory in a semi-quantitative way, it fails to explain as yet the differences in the A factors found for the several reactions studied. Perhaps such an explanation cannot even be hoped for with our present inadequate knowledge of the reaction mechanism, but some suggestions can be offered in the hope that they may lead to more exact calculations in the future. As has been shown in several recent publications,⁵⁶⁻⁵⁸ the assumption of internal free rotation leads to too high entropy values for saturated hydrocarbons. Hence in the present calculations, numerically smaller partition functions should also be used. The extent of the lowering, however, is uncertain and undoubtedly it would be incorrect to assume that it is the same for the several structures considered. Thus, in 1,3-butadiene—and other conjugated diene hydrocarbons—a resonance energy between the double bonds has been found which amounts to some 3 Cal. per mole.¹⁴ This resonance tends to keep the double bonds in a plane and hence offers additional hindrance to free rotation above that which is due to causes operative in saturated hydrocarbons.

⁵⁵ In which vibrational (or rotational) partition functions in the denominator of the rate expression are assumed to cancel an equal number of vibrational (or rotational) functions in the numerator.

⁵⁶ Smith and Vaughan, *J. Chem. Phys.* **3**, 341 (1935).

⁵⁷ Aston, *ibid.* **4**, 391 (1936).

⁵⁸ Kemp and Pitzer, *ibid.* **4**, 749 (1936); *J. Am. Chem. Soc.* **59**, 276 (1937).

It is possible that this effect may cause the denominator of the rate expression in 1,3-butadiene polymerization to be smaller than that in the Diels-Alder condensations thereby explaining the experimental differences in the A factors; however, in acrolein or crotonaldehyde the experimental resonance energy is hardly smaller than in 1,3-butadiene (work from this laboratory to be published in the near future). The activated complexes in the two groups of reactions are so similar—differing only in side structures which do not take an active part in the reaction—that one meets considerable difficulty in trying to find a reasonable explanation of the observed difference. But the same difficulty arises with the cyclic complex and so this point cannot decide the issue.

The polymerization of cyclopentadiene is better suited to a numerical calculation because of lesser uncertainties due to internal rotations. Using the tricyclic dimer with conventional internuclear distances for the model of the activated complex, one finds for the average frequency of the six new vibrations $\nu \leq 150 \text{ cm}^{-1}$, while the free radical model leads to $\nu \leq 450 \text{ cm}^{-1}$ in the approximation defined in reference 55. This latter figure is to be lowered if there is no free rotation around the single bond joining the two rings and in any case is much more reasonable than the other.⁴³ Qualitatively one can explain why the A factor of this reaction is smaller than those of other diene reactions: long straight chains are formed there with resultant lowering of the vibrational frequencies, whereas here the two rings retain their dynamic independence fairly well and hence have essentially the same frequencies as before the reaction.⁵⁹

It may be pointed out that for most of the organic compounds which are known to polymerize readily, free radical intermediates, stabilized by resonance, can be constructed. It is therefore probable that this particular mechanism has a greater range of application than merely in diene polymerization and Diels-Alder condensation.

⁵⁹ If the new work of Khambata and Wassermann (reference 42) is correct, the cyclopentadiene reaction is more similar to the Diels-Alder reactions. The explanation as given is still applicable for this particular reaction.

In having outlined these interpretations we are fully aware of their crudeness and approximate character. However, the essential point to be noted is that the use of cyclic intermediary complexes does not reduce the difficulties of interpretation but actually increases them greatly. Because of this and of other evidence, we believe the free radical mechanism in these polymerizations to be more probable.

We are indebted to Dr. William E. Vaughan of this laboratory for several valuable suggestions and for assistance with some of the measurements.

SUMMARY

Dimerizations of styrene, vinyl acetylene, chloroprene, vinyl acetate, allene, cyclopentadiene, 1,3-pentadiene and 2,3-dimethyl butadiene-1,3 have been studied in the gas phase. Only the last three reactions give clean-cut results; their rate data can be represented by:

1,3-pentadiene

$$k = 3.5 \times 10^{10} \exp(-26000/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1}$$

2,3-dimethyl butadiene-1,3

$$k = 1.4 \times 10^{10} \exp(-25300/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1}$$

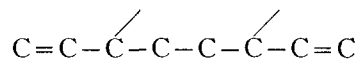
cyclopentadiene

$$k = 8.5 \times 10^7 \exp(-14900/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1}$$

The dimerization of the last compound has also been studied in the pure liquid phase and in tetrahydronaphthalene solution. The rates can be represented by the equations: $k = 2.0 \times 10^9 \exp(-17100/RT)$ and $k = 4.2 \times 10^9 \exp(-17300/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1}$.

The depolymerization of dicyclopentadiene has been studied in the gas phase. The reaction is unimolecular and the rate may be expressed by: $k = 1.0 \times 10^{13} \exp(-33700/RT) \text{ sec.}^{-1}$.

The kinetics of the gas phase polymerizations and Diels-Alder condensations are discussed and it is concluded that they occur through the mechanism of free radicals. In the case of 1,3-butadiene the radical has the structure:



which is stabilized by resonance between four possible electronic structures.