The system of which the sulfonated rosindone is the oxidant gave electrode potentials which may be described by the equation

$$E_h = E_0 - 0.03006 \log [\mathrm{S_R}]/[\mathrm{S_O}] - 0.03006 \log \left[K' + \sqrt{K'_2 + 8K'[\mathrm{S_O}]}\right]/2K' + 0.03006 \log [K'_{r_1}K'_{r_2}(\mathrm{H^+}) + K'_{r_1}(\mathrm{H^+})^2 + (\mathrm{H^+})^3]$$

$K'_{r_1} = 3.2 \times 10^{-8}$ ($pK'_{r_1} = 7.5$); $K'_{r_2} = 3.2 \times 10^{-10}$ ($pK'_{r_2} = 9.5$). K' is the apparent dissociation constant for an equilibrium between uni- and bimolecular species. K' is approximately 5×10^{-5} when the dye is in phosphate buffers and 1×10^{-5} when the dye is in borate buffers. This specific salt effect is also reflected in the extrapolated values of E_0, 0.243 for phosphate and 0.251 for borate buffers.

Other evidences of a reversible association of the rosindone in aqueous or aqueous buffer solutions are: (1) the qualitative analysis of the changes in the spectrophotometric absorption curves which follow dilution; (2) the analysis of quantitative studies on the distribution of the dye between water and amyl alcohol. The values of K', estimated by the distribution studies, are in substantial agreement with those estimated by the potentiometric measurements.

When the sulfonated rosindone is 90% reduced, $P_H = 7.0$ (phosphate buffer) and total dye concentration is 3×10^{-5} M, the electrode potential is that of the hydrogen electrode under 1 atmosphere of hydrogen. This system gives potentials nearer that of the hydrogen electrode than any system previously reported in this series of papers on oxidation–reduction indicators.

BALTIMORE, MARYLAND

RECEIVED JULY 10, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 369]

The Homogeneous Thermal Polymerization of Isoprene

BY WILLIAM E. VAUGHAN[1]

In an earlier publication[2] there has been reported an investigation of the homogeneous thermal polymerization of 1,3-butadiene, and in that paper there has been given a brief review of the several similar reactions hitherto studied, together with a cursory survey of some of the theoretical aspects of the general problem of association processes. There is thus no need to repeat that material. Suffice it to say that Kassel's contention[3] that the formation of polyatomic molecules by a second-order association process is possible at a relatively large fraction of all collisions, is well supported by the experimental evidence thus far presented. It may also be mentioned that the data for the three reactions considered, namely,

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[1] National Research Fellow in Chemistry.

[2] Vaughan, THIS JOURNAL, **54**, 3863 (1932).

[3] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., N. Y., 1932, pp. 44–47; also THIS JOURNAL, **53**, 2143 (1931).

the hydrogenation of ethylene and the dimerizations of ethylene and of 1,3-butadiene, show that the ratio of the empirical second-order rate constant to that calculated from the collision frequency and the simple Maxwellian factor decreases for the reactions in the order named; this was interpreted as indicating that orientation of the properly activated particles at the moment of impact was highly important for the achievement of reaction, and that the more complex the molecules the more precise must be their mutual locations.

The present study is a continuation of the former, concerning itself with the 2-methyl derivative of 1,3-butadiene, which is known to form a dimer under certain conditions.

Experimental

The technique employed was essentially the same as that used previously. The furnace was electrically heated and its temperature manually maintained at constancy. Temperatures were determined by means of a calibrated thermometer. It is estimated that the temperature readings were accurate to ±1°. During the first several hours of all runs the variation of the temperature was within ±0.5°. The reaction cells, several of which were used, were all of 80 cc. capacity; they communicated through capillary tubing to the supply of isoprene and to a quartz spiral manometer. In those experiments where the pressure was sufficiently high so that isoprene would condense out in the tubing at the temperature of the room, the entire reaction system other than the cell, namely, the tubing and spiral manometer, was electrically heated to approximately 150°, and in such cases the reaction system was sealed off from the auxiliary trap used in conjunction with the storage vessel for the admittance of the isoprene. A mercury column served as an absolute manometer in combination with the quartz spiral which acted as a null instrument; the scale of the former was readable by means of a vernier with a precision of 0.1 mm. This figure likewise is a close estimate of the accuracy with which the fibers of the quartz spiral were adjustable.

The reactant was an Eastman Kodak Company product which was used without further chemical treatment. It was, however, fractionally distilled *in vacuo* several times, only the middle portion being preserved. In the course of the experiments two separate samples were utilized with no detectable difference in their behavior.

Data and Results

In the several runs performed observations were made of the pressures at various time intervals, chosen to correspond to approximately equal amounts of reaction. These data when plotted gave curves of the types shown in Fig. 1. The curves possessing a minimum are characteristic of all of the higher temperature experiments (above 371°), while the continuous downward trend of pressure with time shown by No. 26 of the figure is typical of rate measurements made at temperatures from 286.5 to 371°. It is these latter rates which are primarily of interest to the purposes of this study.

A number of reports[4] confirm the thermal dimerization of *liquid* isoprene,

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[4] (a) Lebedev, *J. Russ. Phys.-Chem. Soc.*, **62**, 1395 (1930); **45**, 1249 (1913); (b) Harries, *Ann.*, **383**, 206 (1911); (c) Ostromuislenski, *J. Russ. Phys.-Chem. Soc.*, **47**, 1928 (1915); (d) Aschan, *Ann.*, **439**, 221 (1924); *Ber.*, **57**, 1959 (1924); (e) Wagner-Jauregg, *ibid.*, **488**, 176 (1931); (f) Whitby and Crozier, *Canadian J. Research*, **6**, 203 (1932).

although there is some disagreement as to the nature of the dimer formed; the recent work indicates that the product is a monocyclic compound. Gapon[5] has investigated the kinetics of the polymerization of liquid isoprene at 100–150° and claims to have differentiated three second-order reactions that occur simultaneously; two dimers, dipentene and 1,3-dimethyl-1-vinylcyclohexene-3, are formed together with a complex polymer. These three processes are seemingly so clearly differentiated that he further gives as the activation energies for the three reactions, 22,400, 21,500 and 18,800 calories, respectively. In the light of the experimental difficulties involved, the precision of these results is very surprising.

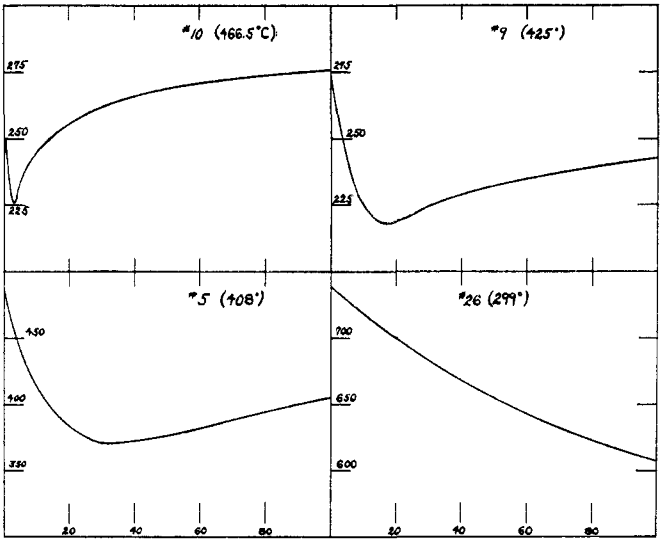

Fig. 1.—Pressure (mm.) *vs.* time (min.).

The above-mentioned results and the analogous study of butadiene obviously suggest a treatment of the pressure–time data by appplication of the integrated second-order reaction rate equation

$$k = \Delta p_I / (\Delta t)(p_{I_1})(p_{I_2}) \qquad (1)$$

wherein Δp_I is the change in isoprene pressure in the interval Δt, $(t_2 - t_1)$, and p_{I_1} and p_{I_2} are the pressures of isoprene at the times t_1 and t_2. The results to which this leads are shown by Table I, which shows the rate constants, k, at various fractions of isoprene converted for Run No. 24, which was chosen as typical of the low temperature runs, and by Fig. 2, which shows a plot of such a set of data for a similar experiment.

The downward trend of k with time considered in relation to the behavior revealed in the higher temperature experiments, namely, that a pressure increase occurs after a certain pressure decrease, may be taken to indicate

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[5] Gapon, *J. Russ. Phys.-Chem. Soc.*, **62**, 1395 (1930); *J. Gen. Chem.* (U. S. S. R.), **1**, 1177 (1931).

TABLE I

RUN 24. INITIAL PRESSURE, 620.0 MM.; TEMP., 299.5°

Fraction of isoprene converted	k (mm.$^{-1}$ min.$^{-1}$) $\times 10^5$	Fraction of isoprene converted	k (mm.$^{-1}$ min.$^{-1}$) $\times 10^5$	Fraction of isoprene converted	k (mm.$^{-1}$ min.$^{-1}$) $\times 10^5$
0.080	(0.802)	0.292	0.773	0.497	0.593
.104	.834	.316	.763	.519	.589
.126	.817	.340	.738	.550	.627
.145	.834	.361	.695	.579	.569
.162	.872	.384	.699	.612	.553
.187	.861	.414	.679	.658	.488
.217	.820	.430	.624	.708	.487
.237	.824	.449	.607	.798	.418
.263	.820	.474	.603		

the presence of a subsequent decomposition of the dimer, occurring along with the formation process. Certain runs were prolonged, such as No. 5 at 408°, and it was observed that the final pressure (attained after 1080 min.) was the same as the initial pressure; it would seem, then, that one molecule of the dimer decomposes to give two molecules of gaseous products. However, in the highest temperature experiments (for example, No. 10), the final pressure exceeded the initial, indicating still further decomposition. The products of the decomposition were probably unsaturated hydrocarbons, inasmuch as freezing down with liquid air caused the pressure to drop to an unreadable amount, indicating that no hydrogen is split out. The cool cell, after the furnace was removed following the termination of a run, contained droplets of a colorless liquid condensate which had a definitely turpentine-like odor, somewhat similar to that of limonene. This material rapidly decolorized a few drops of a very dilute permanganate solution, as does limonene. In none of the lower temperature experiments was any discoloration of the cell observed but at the higher temperatures a dark film appeared on the walls.

To secure a rate constant representative of the polymerization reaction alone, undisturbed by the decomposition, the data of each run were treated as shown in Fig. 2, the constant obtained by extrapolation to zero fraction converted being taken as the true rate of the association. The construction of the straight line through the divergent points can be none too precise and the constants are certainly liable to some error. The results obtained are listed in Table II.

It may be recalled that in the case of butadiene[6] the rate constant was obtained in a similar fashion; but the extrapolation was simpler, since the constants for the intervals were invariant until 60–70% conversion was approached, at which point the constants increased, due seemingly to further polymerization, in contrast to the present steady decrease of the constants from the onset of reaction. Table II shows that in the small pressure range utilized the rate is independent of pressure

(6) See Fig. 1, p. 3867, of Ref. 2.

TABLE II

SUMMARY OF DATA

Run	Temp., °C.	Init. press., mm.	Fraction converted	*k* (mm.$^{-1}$ min.$^{-1}$ $\times 10^{+5}$)	*k* (cc. moles^{-1} sec.$^{-1}$)	Comment
11	371	223.3	0.442	$14._8$	$93._8$	
12	358	225.0	.678	7.9_0	$51._8$	
13	349	212.1	.726	5.1_5	$33._3$	
14	358	246.1	.567	6.0_0	$41._1$	Packed
15	323.5	214.2	.482	1.7_8	$11._1$	
16	323.5	424.0	.635	1.8_7	$11._6$	Packed
17	329.0	305.0	.420	2.5_2	$15._8$	
18	297.5	316.0	.453	0.79	4.6_8	
19	300.5	314.1	.559	.86	5.1_2	Hexaphenylethane
20	286.5	408.5	.527	.42	2.4_4	Hexaphenylethane
21	286.5	312.0	.487	.42	2.4_4	Hexaphenylethane; packed
22	301.0	289.4	.586	.92	5.4_8	Hexaphenylethane; packed
23	300.0	412.4	.726	.81	4.8_3	
24	299.5	620.0	.798	.93	5.5_3	
25	297.0	615.0	.776	.70	4.1_5	
26	299.0	739.0	.470	.83	4.9_4	

It is to be further observed that in certain of the runs, such as No. 21, shown in Fig. 2, at the beginning of the reaction there was a brief period during which there was an abrupt decrease in the values of the constants to a point where they revealed the apparent linear relationship to the fraction of isoprene converted (as was utilized in determining the rate at zero percentage conversion). It was thought that this somewhat anomalous feature might be due to an extraneous reaction such as might be

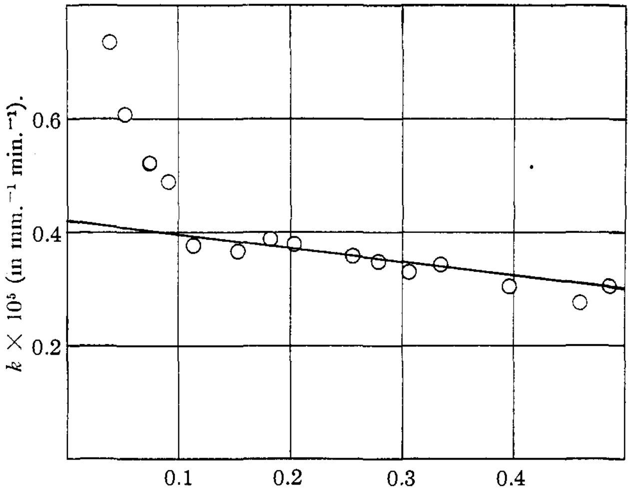

Fig. 2.—Run 21 (286.5°).

brought about by traces of peroxides in the gas, causing a catalyzed polymerization. Conant and Peterson[7] have proved in their very high pressure polymerizations of isoprene that traces of peroxides are extremely active catalysts in the process and that by treatment of the liquid reactant with hexaphenylethane the rate was reduced ten-fold. This procedure was tried in the cases of Runs 19 to 22, and this initial effect was diminished but not completely removed.

The reaction seemed to be essentially homogeneous, inasmuch as in a cell packed with lengths of Pyrex tubing so that the surface–volume ratio was increased five-fold, it proceeded with the same velocity as in the "empty" cell.

An effort was made to express quantitatively the data for the higher temperature experiments. Computation showed that in the earlier part of a given run the rate was well expressed by the simple second-order equation (1). Attempts were then made to express the total pressure over the whole range of the run as resulting from a concurrent bimolecular association and a first- or second-order decomposition of the dimer formed, but the complexity of the mathematical analysis coupled with the uncertainty of the premises led to the pigeon-holing of this phase of the problem pending further investigation.

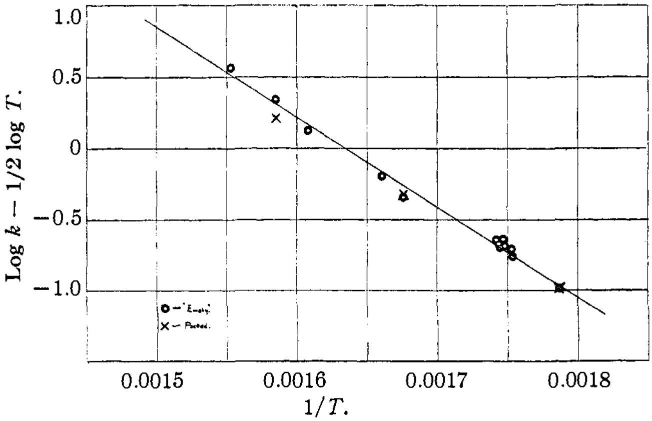

Fig. 3.

A plot of $\log_{10} k - 1/2 \log_{10} T$ *vs.* $1/T$ (k in cc. moles^{-1} sec.$^{-1}$), (in accord with the equation $k = AT^{1/2} e^{-E/RT}$), is shown in Fig. 3. The slope of the line corresponds to $E = 28{,}900$ calories and an equation expressing it is $k = 2.193(10^{10})\, T^{1/2} e^{-28{,}900/RT}$.

Discussion of the Results

Following the method used previously[8] it is possible to determine the efficiency of molecule formation at collisions between properly activated

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[7] Conant and Peterson, THIS JOURNAL, **54**, 628 (1932).

[8] Ref. 2, p. 3873.

particles. For molecules possessing in one degree of freedom an energy of 28,900 calories per mole at 570°K. the Maxwellian factor is 7.83×10^{-12}. The total number of collisions per cc. in each second is given by[9] $Z = 2N^2\sigma^2\sqrt{\pi kT/m}$, wherein N is the number of molecules of diameter σ and mass m per cc. Evaluation of Z for C_5H_8 at a concentration of one mole per liter for a temperature of 570°K. on the assumption of a diameter of 5.0×10^{-8} cm. gives 8.57×10^{31}. If molecules of the dimer resulted on each collision of properly activated molecules, the rate of disappearance of isoprene should be calculable from $2Z$ times the exponential, since two molecules react at each successful impact; this product is 2.21 (units of moles/liter and sec.). The value of the experimentally determined constant at this temperature is 4.15×10^{-3}, expressed in the same units. The ratio of these two figures is 1:530. The significance of this figure as bearing upon the orientation of the particles on collision has been treated heretofore in the discussion of the reaction mechanism for the association of polyatomic molecules.

In Table III are summarized some data for the four second-order association reactions treated to date. In the last column are given the ratios which show conclusively the validity of Kassel's argument, based on theory, for the possibility of the occurrence of such processes with a reasonably high efficiency. That the ratios are not regularly decreasing with increasing complexity of the molecules involved, as might be required by the simple *a priori* picture of a "steric factor," is not unexpected, inasmuch as the "steric factor" may well be a predominating influence and yet be modified by other variables in such complex processes as the formation

TABLE III

SUMMARY OF BIMOLECULAR ASSOCIATION REACTIONS[a]

	Reaction	Ref.	Temp. range, °C.
1	$H_2 + C_2H_4 = C_2H_6$	*b*	475 -550
2	$2C_2H_4 = C_4H_8$	*c*	350 -500
3	$2C_4H_6 = C_8H_{12}$	2	326 -388
4	$2C_5H_8 = C_{10}H_{16}$	. .	286.5-371

	E, cal.	k (liter. moles^{-1} secs.$^{-1}$) Theoretical	k (liter. moles^{-1} secs.$^{-1}$) Experimental	Ratio
1	40,300	2.46	0.0114 (698°K.)	1/220
2	35,700	0.589	.00159 (773°K.)	1/370
3	25,300	273.0	.0265 (614°K.)	1/10,300
4	28,900	2.21	.00415 (570°K.)	1/530

[a] In this table the data of Pease under references *b* and *c* have been recalculated in accordance with the form of the equation $E = AT^{1/2}e^{-E/RT}$; likewise a small error in the value of the average diameter of the molecule used in *b* has been adjusted.

[b] Pease, THIS JOURNAL, **54**, 1876 (1932).

[c] Pease, *ibid.*, **52**, 1158 (1930); **53**, 613 (1931).

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(9) Tolman, "Statistical Mechanics," Chemical Catalog Co., Inc., N. Y., 1927, p. 242.

of the dimer (or possibly mixture of dimers) encountered here, and that met with in the butadiene experiment.

Acknowledgment.—The author is pleased to acknowledge his indebtedness to the Gates Laboratory for the hospitality and facilities extended him, and to his associates there for aid during his stay in Pasadena.

Summary

The homogeneous thermal polymerization of isoprene has been investigated in the temperature range of 286.5 to 371° at pressures varying from 212 to 739 mm.; the principal process is interpreted as a bimolecular association reaction, the rate of which is expressible by $k = 2.193(10^{10}) T^{1/2}e^{-28,900/RT}$.

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RECEIVED JULY 11, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE ZOÖLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Dielectric Constants: Ethanol–Diethyl Ether and Urea–Water Solutions between 0 and 50°

BY JEFFRIES WYMAN, JR.

The importance of a knowledge of the dielectric constant of the solvent as well as its change with temperature in the study of solutions is well known and requires no elaboration. The present paper is a report of routine measurements at a variety of temperatures on two sets of solvents of considerable use especially in organic and biological chemistry. The first set, consisting of mixtures of ethanol and diethyl ether, covers a range of dielectric constant from about 4 to 28. The second, comprising aqueous solutions of urea of concentrations running up to nearly 8 moles per liter, is characterized by dielectric constants greater than that of water, in fact approaching 108 at the upper limit. In this respect the urea–water solutions occupy an exceptional position and afford a convenient class of solvents of high dielectric constant. In fact, apart from certain ampholytes supposed to exist as zwitter ions and one or two compounds closely related to it, urea is the only substance known to form solutions of dielectric constant greater than that of water.[1] Existing data on the dielectric constant of both the above sets of liquids are somewhat incomplete and contain inconsistencies. The present results serve to extend the list of mixed solvents of accurately known dielectric properties such as those dealt with in recent papers by Åkerlöf[2] and Wyman.[3]

(1) See Devoto, *Gazz. chim. ital.*, **61**, 897 (1932); also Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933); **55**, 915 (1933).

(2) Åkerlöf, *ibid.*, **54**, 4125 (1932).

(3) Wyman, *ibid.*, **53**, 3292 (1931).