tion with carbon number appears to increase as the incorporation decreases. For example, the ratio of the peak activity to the C_2 activity (a measure of the variation) is 1.29 and 1.45, in runs H7 and H19, whereas the incorporation is 18 and 7.2%, respectively. This suggests that when the normal synthesis is least disturbed by the added alcohol the variation of radioactivity with carbon number is most pronounced. For the most part, however, the activity is fairly constant (~ ±20%) so that the simple hypothesis advanced by Kummer and Emmett[1] is probably close to the truth. These shortcomings of the theory do suggest, however, that even though the alcohol-type complexes are the principal chain initiators, some other species are also capable of acting in a similar capacity.

The nature of the chain initiator is indicated by the results obtained by Kummer, *et al.*[2] They found that 90% of the propane formed in ethanol tracer runs appeared to be obtained by addition to the α carbon atom of the methylene-labeled ethanol, and the remainder by the addition to the β-carbon atom. It was also established that the hydroxyl group of the unreacted ethanol had not migrated to the unlabeled carbon atom. Thus, it appears that a small fraction of the ethanol reacted to form some species *in which the two carbons were indistinguishable* and which could also build-in to form higher hydrocarbons. Clearly, this suggests that ethylene formed by the dehydration of ethanol is capable of build-in over iron catalysts to form higher hydrocarbons. This has been known to be the case with cobalt catalysts for some time[15] and the present authors have shown that when radioactive ethylene is introduced into the synthesis stream some build-in occurs.[7] Thus, the results with propane suggest that 80% of the propane comes from ethanol with all the addition taking place on the labeled (methylene) carbon atom and 20% of the propane comes from radioactive ethylene with the addition to the labeled carbon occurring only 50% of the time. It seems probable that this effect contributes heavily to the above-mentioned skewing of the radioactivity *vs.* carbon number curves.

In conclusion, it should be emphasized that the mechanism of synthesis appears to be complex, with two or more intermediates functioning as chain initiators. In spite of this, however, the mechanism suggested by Storch, *et al.*,[3] and Kummer, *et al.*,[1] is probably the predominant one operating in the synthesis over iron catalysts and is capable of explaining many of the observed facts.

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[15] R. B. Anderson, ref. 14, p. 317.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Free Radical Initiated Polymerization of Gaseous Unsaturated Hydrocarbons[1]

BY LESLIE C. LANDERS AND DAVID H. VOLMAN

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Methyl radicals from thermally decomposing di-*t*-butyl peroxide were found to initiate the polymerization of gaseous acetylene, 1,3-butadiene, ethylene and propene in the temperature range 130–165°. The rate of polymerization of each unsaturated hydrocarbon was proportional to the first power of the concentration of monomer and to the square root of the concentration of di-*t*-butyl peroxide. This is consistent with a three-step polymerization mechanism consisting of initiation by a unimolecular split of the peroxide into free radicals, propagation by addition of radicals to a multiple bond and termination by radical combination. From a consideration of the relationship between the activation energies of chain initiation, propagation and termination, and of the known values of the activation energies for initiation and termination, the activation energies for propagation of polymerization of acetylene, butadiene, ethylene and propene were determined to be 5.1, 4.9, 8.2 and 5.6 kcal./mole, respectively.

Introduction

Few of the studies of the polymerization of the simpler unsaturated hydrocarbons in the gas phase have been concerned with obtaining values of the activation energies for the chain propagation reactions or, alternatively, for the addition of atoms or radicals to the multiple bond. Raal and Danby[2] reported 6.8 kcal./mole as the activation energy for propagation of ethylene polymerization initiated in the gas phase by methyl radicals. James and Steacie[3] give a preliminary value of 6–8 kcal./mole as the activation energy for the addition of ethyl radical to heptene-1. Volman[4] initiated the polymerization of butadiene by the thermal decomposition of di-*t*-butyl peroxide and reported 2.6 kcal./mole for the propagation activation energy. Volman and Graven[5] later initiated butadiene polymerization by the photolysis of di-*t*-butyl peroxide and acetone and reported 5.4 kcal./mole for the propagation activation energy, in good agreement with Gee's value of 5.5 kcal./mole for the propagation step in the gas phase mercury-photo-sensitized polymerization of butadiene,[6] and the estimate of White and Winkler[7] of 5 kcal./mole for the addition of a hydrogen atom to butadiene. More recently,

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[1] Based on a portion of a thesis presented by L. C. Landers in partial satisfaction of the requirements for the degree of Doctor of Philosophy in the University of California.

[2] F. A. Raal and C. J. Danby, *J. Chem. Soc.*, 2219 (1949).

[3] D. G. L. James and E. W. R. Steacie, unpublished work cited in E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1954, p. 581.

[4] D. H. Volman, *J. Chem. Phys.*, **19**, 668 (1951).

[5] D. H. Volman and W. M. Graven, THIS JOURNAL, **75**, 3111 (1953).

[6] G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

[7] W. H. White and C. A. Winkler, *Can. J. Research*, **26B**, 3 (1948).

Mandelcorn and Steacie[8] reported values of the activation energies for the addition of methyl radical to unsaturated hydrocarbons: acetylene 5.5 kcal./mole, ethylene 7.0 kcal./mole, propene 6.0 kcal./mole and butadiene *ca.* 2.5 kcal./mole.

Previous studies[4,5] in this laboratory of butadiene polymerization have involved initiation by the thermal and photochemical decompositions of di-*t*-butyl peroxide, which occur according to the well known mechanism[5,9,10]

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO \qquad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \qquad (2)$$

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (3)$$

The thermal initiation technique is very convenient, since the peroxide decomposes at a readily measurable rate at 125°. It is assumed that the *t*-butoxy radical formed in (1) decomposes rapidly by (2) at temperatures at which the peroxide decomposes, thus di-*t*-butyl peroxide is a convenient source of methyl radicals at temperatures well below those at which the direct thermal polymerization of unsaturated hydrocarbons takes place.

In the present work this technique was extended to the initiation of polymerization of gaseous acetylene, butadiene, ethylene and propene.

Experimental

The di-*t*-butyl peroxide, kindly donated by the Shell Chemical Corporation, was of unspecified purity. It was deaerated and distilled bulb-to-bulb on the high vacuum line and the middle fraction was retained and stored over Dry Ice. Its refractive index ($n^{20}D$) was 1.3888, which compares well with published values of 1.3888,[5] 1.3889[9] and 1.3890.[10] The acetylene was Matheson Purified Grade, the 1,3-butadiene was Matheson Extra Pure Grade, and the ethylene and propene were Matheson C.P. Grade. Samples of these were condensed and distilled bulb-to-bulb on the high vacuum line, the middle fractions of each being retained. The ethylene was stored over liquid air, and the acetylene, butadiene and propene over Dry Ice.

The polymerizations were carried out in a one-liter Pyrex bulb immersed in an oil-bath thermostat. The temperature was maintained constant to within ±0.05°. Pressure changes during polymerization were measured by a mercury manometer.

Results and Discussion

Di-*t*-butyl peroxide was decomposed at various temperatures in the range 124–177°, and the first-order rate constant obtained was $k_i = 1.6 \times 10^{16} e^{-38.4/RT}$ sec.$^{-1}$, which is within the range of previously reported values.[10–12]

The kinetic data obtained from the polymerization experiments are shown in Tables I–IV. The rates of pressure change given are the initial rates. The values of *k* were calculated from

$$-\frac{dp}{dt} = k(M)(C)^{1/2} \qquad (4)$$

where (M) is the pressure of monomer and (C) is the pressure of di-*t*-butyl peroxide.

It is seen that in each case the rate of pressure change in the system is given by eq. 4. This is of the expected form for a free radical initiated polymerization involving initiation *via* a unimolecular

TABLE I

RATE OF POLYMERIZATION OF ACETYLENE

C_2H_2, mm.	DTBP, mm.	$-dp/dt$, mm./min.	k, mm.$^{-1/2}$ sec.$^{-1}$ × 10^4
	131.8°		
53.2	6.8	0.023	1.7
74.4	7.0	.033	1.7
103.2	6.7	.043	1.6
129.4	7.1	.055	1.6
140.0	6.9	.060	1.6
	149.6°		
61.9	5.7	0.078	5.3
112.1	5.7	.16	6.0
160.2	5.7	.21	5.5
213.7	5.7	.28	5.5
275.7	5.7	.36	5.5
176.9	12.6	.37	5.9
181.9	2.1	.14	5.3
89.3	0.85	.043	5.3
	164.9°		
139.8	4.6	0.46	15.3
208.3	4.7	.69	15.3
274.3	4.9	.91	14.9
66.8	2.7	.19	17.2
303.9	0	0	

TABLE II

RATE OF POLYMERIZATION OF BUTADIENE

C_4H_6, mm.	DTBP, mm.	$-dp/dt$, mm./min.	k, mm.$^{-1/2}$ sec.$^{-1}$ × 10^4
	129.4°		
120.9	14.0	0.015	0.33
215.3	14.0	.025	.31
321.2	14.0	.039	.32
	140.5°		
110.6	15.3	0.030	0.69
167.2	15.3	.047	.71
353.2	15.3	.10	.72
	151.0°		
61.2	14.2	0.037	1.6
116.6	14.2	.064	1.5
154.6	14.2	.087	1.5
178.4	14.2	.083	1.2
296.2	14.2	.15	1.3
408.9	14.2	.24	1.6
413.8	14.2	.22	1.4
281.9	11.7	.14	1.5
288.4	9.1	.13	1.5
296.7	3.9	.085	1.4
296.5	1.1	.042	1.4
217.2	0	0	
	166.2°		
95.6	14.4	0.13	3.6
167.9	14.4	.24	3.8
220.3	14.4	.32	3.8
221.3	14.4	.33	3.9
277.1	0	0	

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[8] L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 474 (1954).

[9] L. M. Dorfman and Z. W. Salsburg, THIS JOURNAL, **73**, 255 (1951).

[10] J. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88, 1336 (1948).

[11] J. Murawski, J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, **19**, 698 (1951).

[12] R. K. Brinton and D. H. Volman, *ibid.*, **20**, 25 (1952).

TABLE III

RATE OF POLYMERIZATION OF ETHYLENE

C_2H_4, mm.	DTBP, mm.	$-dp/dt$, mm./min.	k, mm.$^{-1/2}$ sec.$^{-1}$ × 10^4
	131.2°		
140.6	6.6	0.026	0.72
221.8	6.9	.0415	.71
285.1	7.0	.053	.70
290.2	7.0	.057	.74
356.2	7.0	.0655	.70
348.1	14.0	.089	.68
	146.0°		
224.6	7.1	0.14	2.3
289.5	7.0	.18	2.4
364.8	7.1	.22	2.3
422.7	14.1	.36	2.3
146.2	5.6	.094	2.7
195.0	2.8	.074	2.3
	160.1°		
122.8	5.7	0.16	5.5
199.8	5.7	.315	6.6
269.7	5.7	.44	6.8
364.2	5.7	.57	6.6
211.0	4.3	.27	6.2
137.3	2.9	.16	6.9
247.6	0	0	

TABLE IV

RATE OF POLYMERIZATION OF PROPENE

C_3H_6, mm.	DTBP, mm.	$-dp/dt$, mm./min.	k, mm.$^{-1/2}$ sec.$^{-1}$ × 10^4
	135.8°		
146.5	14.1	0.016	0.29
219.3	14.1	.022	.27
286.2	14.1	.030	.28
358.7	14.1	.365	.27
	147.9°		
215.3	14.2	0.049	0.60
286.2	14.2	.070	.65
359.0	14.2	.089	.66
432.3	14.1	.11	.68
286.8	10.4	.061	.66
250.9	7.1	.044	.66
290.0	3.5	.035	.65
290.1	1.0	.018	.62
	160.2°		
295.4	11.4	0.14	1.4
346.0	11.4	.17	1.5
384.9	11.4	.19	1.5
217.4	7.1	.087	1.5
194.4	0	0	

formation of free radicals, polymer growth by addition of radicals to monomer molecules and termination by bimolecular interaction of free radicals.[4] Since it has been shown that negligible amounts of ethane are formed when di-*t*-butyl peroxide is decomposed in the presence of butadiene,[4] it was assumed that each methyl radical formed adds to a monomer molecule, the polymerization proceeding as

$$(CH_3)_3COOC(CH_3) \xrightarrow{k_i} 2CH_3COCH_3 + 2CH_3\cdot \quad (5)$$

$$CH_3\cdot + M \xrightarrow{k_p} CH_3M\cdot \quad (6)$$

$$CH_3M\cdot + M \xrightarrow{k_p} CH_3M_2\cdot \quad (7)$$

$$CH_3M_x\cdot + CH_3M_y\cdot \xrightarrow{k_t} (CH_3)_2M_{(x+y)} \quad (8)$$

$$CH_3M_x\cdot + CH_3M_x\cdot \xrightarrow{^1/_2k_t} (CH_3)_2M_{(x+x)} \quad (9)$$

This formulation[13] yields, by the usual steady-state treatment

$$\frac{-d(M)}{dt} = k_p\left(\frac{2k_i}{k_t}\right)^{1/2}(M)(C)^{1/2} \quad (10)$$

For the determination of activation energies, the values of k in eq. 4 were calculated from the slopes of the straight lines obtained in plots of $-(dp/dt)/(C)^{1/2}$ *vs.* (M). These values are listed in Table V.

TABLE V

POLYMERIZATION RATE CONSTANTS

T, °C.	k, moles$^{-1/2}$/l. sec.$^{-1}$ × 10^4	T, °C.	k, (moles/l.)$^{-1/2}$ sec.$^{-1}$ × 10^4
Acetylene		Ethylene	
131.8	4.29	131.2	1.86
149.8	15.1	146.0	6.19
164.9	42.0	160.1	18.2
Butadiene		Propene	
129.4	0.85	135.8	0.73
140.5	1.93	147.9	1.77
151.0	3.91	160.2	4.07
166.2	10.5		

The activation energies E corresponding to the slopes in Fig. 1 were calculated to be as follows: acetylene 24.3, butadiene 24.1, ethylene 27.4 and propene 24.8 kcal./mole. Since

$$k = \left(\frac{2k_i}{k_t}\right)^{1/2} k_p \quad (11)$$

then

$$E = E_p + {}^1/_2E_i - {}^1/_2E_t \quad (12)$$

Although it is not possible to estimate E_t from the experimental data, there is abundant evidence that in general E_t is small, not far from zero. The kinetics of the liquid phase photopolymerization of vinyl acetate[14] and methyl methacrylate[15] have been studied by the rotating sector method and E_t was found to be zero in both cases. For the liquid phase benzoyl peroxide initiated polymerization of butyl acrylate, E_t has been found to be zero.[16] The combination of methyl radicals in the gas phase has been found to require no activation

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[13] The justification for taking the termination rate constant for like radicals reacting equal to one-half the rate constant for unlike radicals reacting may be found in collision theory. *Cf.* P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 200.

[14] G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945); *Proc. Roy. Soc.* (*London*), **A189**, 456 (1947).

[15] M. H. Mackay and H. W. Melville, *Trans. Faraday Soc.*, **45**, 323 (1949).

[16] H. W. Melville and A. F. Bickel, *ibid.*, **45**, 1049 (1949).

energy,[17] and an examination of the published data on the reactions of ethyl radicals in the gas phase discloses no good evidence that the activation energy for ethyl radical combination is other than zero.[18] E_t was therefore assigned the value zero for this study, so that

$$E_p = E - {}^1/_2E_i \qquad (13)$$

Using the value of E_i = 38.4 kcal./mole, the values of E_p obtained for the systems studied are: acetylene 5.1, butadiene 4.9, ethylene 8.2 and propene 5.6 kcal./mole. The value for butadiene agrees well with previous values of 5.4[5] and 5.5[6] kcal./mole. The value for ethylene is in fair agreement with the value of 6.8 kcal./mole given by Raal and Danby.[2] However, the results of Raal and Danby depended upon the value of 9.7 kcal./mole for the activation energy for hydrogen atom abstraction from acetaldehyde by methyl radical. If the more recent value of 7.5 kcal./mole given by Volman and Brinton[19] is taken, however, the work of Raal and Danby indicates a value of 4.6 kcal./mole for the propagation activation energy in ethylene polymerization, which does not agree with our results. If the values for E_p obtained in this study are compared with those of Mandelcorn and Steacie previously cited,[8] it is seen that the correspondence is quite good in the cases of acetylene and propene and is certainly within experimental error for ethylene. Since their value for butadiene is a rough approximation, the discrepancy with our value is not significant.

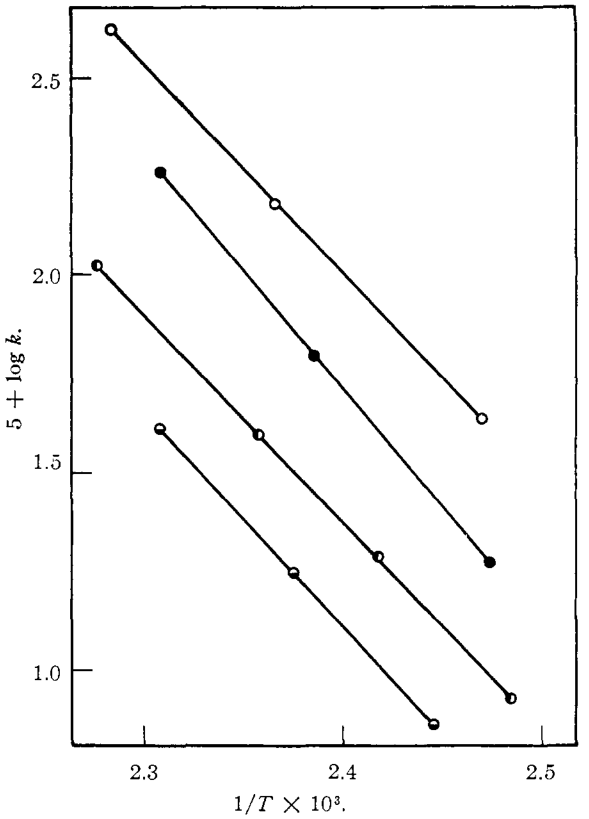

Fig. 1.—Effect of temperature on polymerization rate: ○, acetylene; ●, ethylene; ◐, butadiene; ◒, propene.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for financial aid.

DAVIS, CAL.

[17] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

[18] K. J. Ivin, M. J. H. Wijnen and E. W. R. Steacie, *J. Phys. Chem.*, **56**, 967 (1952).

[19] D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 1952).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The System Ammonia–Hydrazine–Ammonium Chloride

BY FORREST R. HURLEY AND HARRY H. SISLER[1]

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A study of the solid–liquid equilibria in the general ternary system of ammonia, hydrogen chloride and hydrazine was restricted to that portion of the general diagram enclosed in the triangle NH_3–N_2H_4–NH_4Cl, and to pressures near one atmosphere. A ternary compound believed to be $NH_3 \cdot HCl \cdot N_2H_4$, but whose composition has not been established, melts incongruently at −2.5°. The conditions for removal of ammonium chloride from the system by crystallization were outlined.

Sisler and Mattair[2] have shown that hydrazine is formed when chloramine, produced from gaseous chlorine and ammonia, is dissolved in a large excess of liquid ammonia. Subsequent papers from this Laboratory[3] give additional details concerning this synthesis and the recovery of anhydrous hydrazine.

In accordance with the equation

$$ClNH_2 + 2NH_3 = N_2H_4 + NH_4Cl$$

equivalent amounts of hydrazine and ammonium chloride are formed in the reaction. However, the over-all yield of hydrazine is reduced by its reaction with chloramine.

$$2ClNH_2 + N_2H_4 = N_2 + 2NH_4Cl$$

Therefore, the mole ratio of hydrazine to ammonium chloride in the product mixture is always less than unity. During the last stages of evaporation of excess ammonia, hydrazine, which has a lower volatility than ammonia, reacts with ammonium chloride in accordance with the equation

$$N_2H_4 + NH_4Cl = NH_3 + N_2H_5Cl$$

This reaction makes it difficult to distil the hydrazine from the reaction mixture since the ammonium chloride in the mixture is always in excess of the

[1] Department of Chemistry, University of Florida, Gainesville.

[2] R. Mattair and H. H. Sisler, THIS JOURNAL, **73**, 1619 (1951).

[3] H. H. Sisler, *et al.*, *ibid.*, **76**, 3909 (1954); **76**, 3912 (1954); **76**, 3914 (1954).