The acid chloride, 279 g. (2.31 moles), was added dropwise to a mixture of 158 ml. (2.32 moles) of allyl alcohol, 371 ml. (4.6 moles) of pyridine and 500 ml. of toluene. The addition was completed in one hour and gentle reflux was maintained for an additional two hours. The reaction mixture was washed with 2 × 100 ml. water, 3 × 100 ml. 5% hydrochloric acid, 2 × 100 ml. 5% sodium hydroxide and again with 2 × 100 ml. water. After drying over 35 g. of calcium chloride and 15 g. of potassium carbonate, the ester was distilled under nitrogen. The product was collected at 138–140°, refractionated and collected at 138.5–138.7°, n^{25}_{D} 1.4098. The yield was 155 g. (47.5% based on acid chloride, 44.6% based on acid).

Isopropenyl acetate from the Tennessee Eastman Co. was distilled and collected at 96–97°.

Benzoyl peroxide was purified by precipitation with methanol from chloroform solution and with distilled water from acetone solution.

Experimental Procedure.—A solution of benzoyl peroxide in the monomer was transferred by means of a hypodermic syringe to Pyrex tubes with constricted necks. The tubes were cooled in a Dry Ice–methanol-bath and evacuated on a Cenco–Hyvac oil-pump and then flushed with pure, dry nitrogen. Alternate evacuations and nitrogen flushings were repeated several times after which the tubes were sealed under vacuum. The tubes were suspended in a rocking wire basket in a constant temperature bath of paraffin oil maintained at 80 ± 0.1°. At measured intervals tubes were removed and dipped into the freezing mixture. The tubes were opened and samples were removed by hypodermic syringe for determination of peroxide concentration.

The concentration of benzoyl peroxide in the allyl esters was determined by iodometric titration in glacial acetic acid after addition of potassium iodide according to the method of Bartlett and Altschul.[7] The concentration of peroxide in isopropenyl acetate was determined by back titration of excess arsenious oxide with standard iodine according to the method of Siggia.[19]

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[19] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 102.

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[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Allyl Polymerization. III. Kinetics of Polymerization of Allyl Esters[1,2]

BY NORMAN G. GAYLORD[3] AND FREDERICK R. EIRICH

The peroxide-catalyzed bulk polymerization of allyl esters, attended by the phenomenon of degradative chain transfer, may also be accompanied, to a small extent, by secondary reactions, wherein hydrogen abstraction from the acid derived portion of the ester or a free radical displacement reaction occurs. The extent of these reactions determines the degree of further lowering of the $\overline{DP}$ beyond that brought about by the primary degradative attack. The following order of $\overline{DP}$ is found in the allyl esters: trimethylacetate < propionate < acetate < ethyl carbonate. A kinetic scheme is set up including these secondary reactions and the conditions under which it yields the experimentally observed constant dM/dP are discussed. The polymerization of isopropenyl acetate with benzoyl peroxide is almost identical with that of allyl acetate, the shift in the position of the ester group apparently producing little change in polymerization behavior. The reciprocal relation between $\overline{DP}$ and rate of Bz_2O_2 decomposition may be traced to a common cause, *i.e.*, the relative ease of transfer reactions on allylic molecules.

The benzoyl peroxide catalyzed bulk polymerization of allyl acetate at 80° yields a polymer with an average molecular weight of about 1300.[4] In any given polymerization, the concentration of monomer polymerized is, to a good approximation, a linear function of the concentration of peroxide decomposed, *i.e.*, dM/dP is constant. The constancy of dM/dP is attributed to degradative chain transfer[4] wherein active radicals, as in growing chains, yield stabilized radicals with lowered reactivity by abstraction of α-methylenic hydrogen from the allylic monomer. Emulsion polymerization of allyl acetate with potassium persulfate gives a polymer of the same average $\overline{DP}$ as in bulk polymerization indicating analogous initiation and termination mechanisms.[5]

In previous papers[6] it was shown that the decomposition of benzoyl peroxide in allyl alcohol, allyl bromide and several allyl esters was compatible with the existence of a spontaneous unimolecular reaction accompanied by a free radical induced chain decomposition. The present investigation is concerned with a study of the kinetics of the benzoyl peroxide catalyzed polymerization of allyl esters.

Experimental Results

The bulk polymerization of several allyl esters was carried out under vacuum at 80°, in the presence of varying initial concentrations of benzoyl peroxide. The concentrations of monomer and peroxide were followed as a function of time. Unsaturation and peroxide concentration were determined by the methods of Bartlett and Altschul.[4]

The results are summarized in Table I wherein the concentrations are expressed in moles per kilogram.[4] The constant value of dM/dP in a given run and the variation of this value with initial peroxide concentration are shown in Fig. 1.

Discussion

Secondary Degradative Attack.—As indicated by Bartlett and Altschul[4] there are two possible positions in allyl acetate from which hydrogen atoms might be removed to yield a free radical with greater stability than the attacking radical. Bartlett favored reaction 1 and rejected reaction 2 on the grounds that vinyl acetate which can undergo the second reaction but not the first, polymerizes to long chains with no appearance of degradative chain transfer, while allyl propyl

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[2] Abstracted from a portion of the dissertation submitted by Norman G. Gaylord to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

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[4] P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 816 (1945).

[5] P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

[6] N. G. Gaylord and F. R. Eirich; Part I, THIS JOURNAL, **73**, 4981 (1951); Part II, *ibid.*, **74**, 334 (1952).

TABLE I

POLYMERIZATION OF ALLYL ESTERS WITH BENZOYL PEROXIDE AT 80 ± 0.1°

Time, hours	Peroxide (m./kg.)	Monomer (m./kg.)	Polymer, %	Peroxide (m./kg.)	Monomer (m./kg.)	Polymer, %	Peroxide (m./kg.)	Monomer (m./kg.)	Polymer, %
				A. Allyl acetate					
		Bz_2O_2, 2.05%			Bz_2O_2, 4.94%			Bz_2O_2, 9.96%	
0.0	0.0845	9.79	0.0	0.204	9.50	0.0	0.411	8.93	0.0
2.50	.0517	8.80	10.1	.115	7.69	19.1	.198	5.63	36.9
5.00	.0316	8.40	14.2	.0669	6.73	29.2	.109	4.28	52.1
24.00	....	7.40	24.4	....	5.17	45.5	....	2.81	68.5
				B. Allyl propionate					
		Bz_2O_2, 1.97%			Bz_2O_2, 4.94%			Bz_2O_2, 9.52%	
0.0	0.0814	8.67	0.0	0.204	8.25	0.0	0.393	7.75	0.0
2.50	.0488	7.95	8.3	.113	6.86	16.8	.183	5.20	32.9
5.00	.0314	7.60	12.3	.0539	5.96	27.8	.0823	3.91	49.5
24.00	....	6.84	21.1	....	4.46	45.9	....	2.31	70.2
				C. Allyl ethyl carbonate					
		Bz_2O_2, 2.02%			Bz_2O_2, 4.94%			Bz_2O_2, 8.96%	
0.0	0.0836	7.57	0.0	0.204	7.51	0.0	0.370	7.05	0.0
2.50	.0523	6.69	11.6	.119	5.45	27.4	.190	4.17	40.8
5.00	.0334	6.19	18.2	.0727	4.46	40.6	.106	3.00	57.4
24.00	....	4.74	37.4	....	2.98	60.3	....	1.83	74.0
				D. Allyl trimethylacetate					
		Bz_2O_2, 2.08%			Bz_2O_2, 5.05%				
0.0	0.0859	6.84	0.0	0.208	6.70	0.0			
2.50	.0445	6.14	10.2	.1025	5.16	23.0			
5.00	.0240	5.68	17.0	.0520	4.30	35.9			
24.00	....	5.29	22.7	....	3.57	46.7			
				E. Isopropenyl acetate					
		Bz_2O_2, 2.01%			Bz_2O_2, 4.95%				
0.0	0.0830	9.78	0.0	0.205	9.43	0.0			
2.50	.0501	8.92	8.8	.112	7.70	18.4			
5.00	.0308	8.45	13.6	.0643	6.83	27.6			
48.00	....	7.13	27.1	....	4.81	48.9			

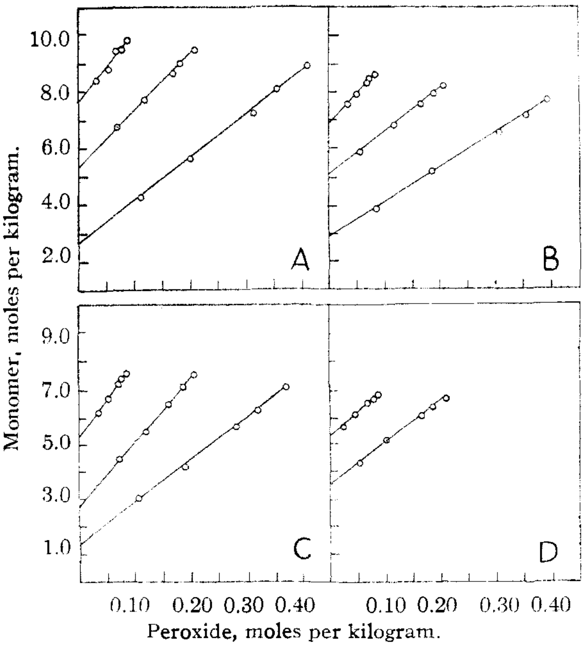
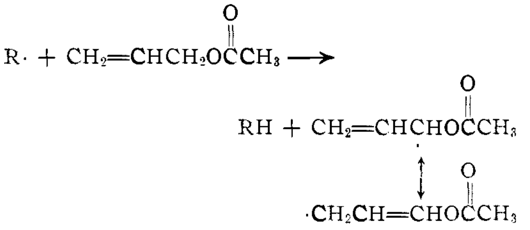
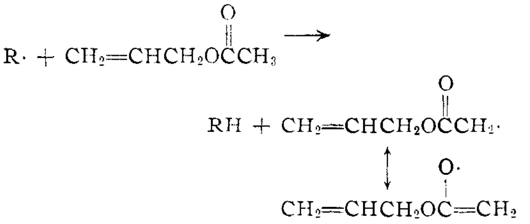


Fig. 1.—Monomer concentration plotted against peroxide concentration in bulk polymerization of allyl esters at 80°: A, allyl acetate; B, allyl propionate; C, allyl ethyl carbonate; D, allyl trimethylacetate. Data from Table I: upper curve, 2% Bz_2O_2; middle curve, 5% Bz_2O_2; lower curve, 10% Bz_2O_2.

carbonate which would undergo the first but not the second reaction shows a constant dM/dP.



$$R\cdot + CH_2{=}CHCH_2O\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow RH + CH_2{=}CH\underset{\cdot}{C}HO\overset{O}{\overset{\|}{C}}CH_3 \updownarrow \cdot CH_2CH{=}CHO\overset{O}{\overset{\|}{C}}CH_3 \qquad (1)$$



$$R\cdot + CH_2{=}CHCH_2O\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow RH + CH_2{=}CHCH_2O\overset{O}{\overset{\|}{C}}CH_2\cdot \updownarrow CH_2{=}CHCH_2O\overset{O\cdot}{\overset{|}{C}}{=}CH_2 \qquad (2)$$

A summary of constants obtained in the bulk polymerization of several allyl esters in the presence of benzoyl peroxide at 80° is given in Table II along with some of the data of Bartlett and Altschul. The relatively small variation in the results supports Bartlett's contention that hydrogen abstraction from the methylene group alpha to the double bond is the primary source of degradative chain transfer. It is difficult to see, however, how a kinetic scheme formulated by the use of

TABLE II

SUMMARY OF CONSTANTS FOR THE POLYMERIZATION OF ALLYL ESTERS BY BENZOYL PEROXIDE AT 80 ± 0.1°

Monomer	Initial wt. peroxide, %	$\overline{DP}$	$\frac{dM}{dP}$	Conversion,[c] %
Allyl acetate	2.05	12.2	25.5	26.1
	4.94	12.6	20.8	46.1
	9.96	12.1	15.2	69.4
		12.3 ± 0.3		
Allyl acetate[a]	1.01	13.5	28.8	12.0
	2.14	13.6	24.4	25.2
	6.10	14.1	18.5	49.0
	9.95	14.0	15.6	70.9
		13.7 ± 0.4[b]		
Allyl propionate	1.97	10.3	22.2	21.1
	4.94	10.6	15.5	45.9
	9.52	9.9	12.3	72.1
		10.3 ± 0.2		
Allyl ethyl carbonate	2.02	14.3	27.7	38.3
	4.94	14.0	24.1	62.7
	8.96	14.7	14.5	74.1
		14.3 ± 0.2		
Allyl trimethylacetate	2.08	5.6	18.7	23.7
	5.05	5.3	15.7	47.5
		5.45 ± 0.15		
Isopropenyl acetate	2.01	12.6	25.1	27.1
	4.95	12.4	18.6	48.9
		12.5 ± 0.1		

[a] Data from Bartlett and Altschul, ref. 4. [b] $\overline{DP}$ obtained from Staudinger's equation after calibration with two samples of M = 890 and 1150, determined cryoscopically. [c] 48 hours.

reaction 1 alone could serve as an explanation for the small but significant deviations which are observed within the series of allyl esters. These variations appear to be indicative of the extent to which these compounds can and do participate in reaction 2 as well as reaction 1.

Independent support for this possibility is found in the result of Matheson, *et al.*,[7] that chain transfer in the methyl group of vinyl acetate is about forty times as frequent as that occurring in the side methyl of methyl methacrylate.[8] Further, in the peroxide-catalyzed polymerization of vinyl acetate the $\overline{DP}$ is < 600 and as many as 100 or more transfer reactions per kinetic chain are indicated.[7] Similarly, the criterion of a constant dM/dP for reaction 1 is not compelling since a mechanism leading to a constant dM/dP can be equally formulated if reactions 1 and 2 coexist. Considering the original scheme of degradative chain transfer, and adding the steps involved in the additional transfer reaction 2, we have

$$\underset{P}{C_6H_5COO{-}OOCC_6H_5} \xrightarrow{k_1} \underset{\rho}{2C_6H_5COO\cdot}$$

$$\underset{\rho}{C_6H_5COO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_a} \underset{R_1}{C_6H_5COOCH_2\underset{\cdot}{C}HCH_2OCOCH_3}$$

$$\underset{\rho}{C_6H_5COO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_b} CO_2 + \underset{R_1}{C_6H_5CH_2\underset{\cdot}{C}HCH_2OCOCH_3}$$

$$\underset{\rho}{C_6H_5COO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_c} C_6H_5COOH + \underset{r}{CH_2{=}CH\underset{\cdot}{C}HOCOCH_3}$$

$$\underset{\rho}{C_6H_5COO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_d} C_6H_5COOH + \underset{\gamma}{CH_2{=}CHCH_2OCOCH_2\cdot}$$

$$R_n + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_2} \underset{R_{n+1}}{RCH_2\underset{\cdot}{C}HCH_2OCOCH_3}$$

$$R + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_3} RH + \underset{r}{CH_2{=}CH\underset{\cdot}{C}HOCOCH_3}$$

$$R + \underset{M}{CH_2{=}CHCH_2OCOCH_3} \xrightarrow{k_4} RH + \underset{\gamma}{CH_2{=}CHCH_2OCOCH_2\cdot}$$

$$\mathrm{r} + \mathrm{r} \xrightarrow{k_5} \mathrm{r} - \mathrm{r}$$

$$\gamma + \gamma \xrightarrow{k_6} \gamma - \gamma$$

$$\mathrm{r} + \gamma \xrightarrow{k_7} \mathrm{r} - \gamma$$

By steady state assumptions we have

$$-\mathrm{d}M/\mathrm{d}t = (k_a + k_b + k_c + k_d)\,\rho M + (k_2 + k_3 + k_4)RM$$

$$\mathrm{d}\rho/\mathrm{d}t = 2k_1P - (k_a + k_b + k_c + k_d)\,\rho M = 2k_1P - k^0\,\rho M \cong 0$$

$$\rho = \frac{2k_1P}{k^\circ M} \text{ where } k^\circ = k_a + k_b + k_c + k_d$$

$$\mathrm{d}R/\mathrm{d}t = (k_a + k_b)\,\rho M - (k_3 + k_4)RM \cong 0$$

$$R = \frac{2(k_a + k_b)k_1P}{(k_3 + k_4)k^\circ M}$$

Therefore

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = 2k_1\left(1 + \frac{(k_2 + k_3 + k_4)(k_a + k_b)}{k^\circ(k_3 + k_4)}\right)P$$

$$-\mathrm{d}P/\mathrm{d}t = k_1P^9$$

and

$$\frac{\mathrm{d}M}{\mathrm{d}P} = 2\left(1 + \frac{(k_2 + k_3 + k_4)(k_a + k_b)}{k^\circ(k_3 + k_4)}\right) = \text{constant}$$

Although this mechanism is undoubtedly an over-simplification, it enables us to obtain an over-all picture of the situation.[10]

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(7) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 2610 (1949).

(8) H. Kwart, H. S. Broadbent and P. D. Bartlett, *ibid.*, **72**, 1060 (1950), have obtained a lower value for the chain transfer constant for vinyl acetate, not in good agreement with that of other workers.

(9) This $k_1 = {}^1/_2\, k_1$ of Bartlett and Altschul, ref. 4, and, as in their scheme, does not include induced decomposition.

(10) As pointed out by the Referee, inclusion of R + R → R_2 in the general scheme does not necessarily affect the ultimate kinetic picture since the $\overline{DP}$ data represent statistical averages and do not deny the presence of some molecules considerably larger than the mean.

On the basis of the above kinetic scheme we are in a position to discuss the experimental data summarized in Table II. Reaction 2 of the degradative chain transfer leads, in allyl acetate, to the radical $-OCOCH_2\cdot$ stabilized by resonance through the carbonyl group. In allyl propionate the corresponding radical $-OCO\dot{C}HCH_3$ would be similarly stabilized, while in allyl ethyl carbonate, as in all allyl carbonates, no radical stabilization by the carbonyl group is possible. Thus, in kinetic terms, there is less degradative chain transfer in the carbonate and consequently a somewhat higher $\overline{DP}$. Further, more monomer is consumed per given initiating radical, *i.e.*, fewer active radicals are wasted by termination in degradative attack, so that a higher dM/dP ensues. A slightly higher conversion follows. By similar reasoning, more degradative chain transfer would occur in the propionate than in the acetate due to the greater stability of the radical formed in the propionate, as borne out by the data of Table II.

Further evidence in favor of degradative attack in the acid derived portion of the ester, in particular on a methylenic hydrogen adjacent to carbonyl, can be observed in the work of Cohen, *et al.*, on allyl chloroacetate.[11] While no molecular weights as such were determined, sufficient values of η_{sp}/c were calculated so as to show (Table III) that the $\overline{DP}$ obtained from allyl chloroacetate must be of the same low order of magnitude as that of the other allyl esters. At the same time it was found that the conversion is much higher for a given amount of peroxide. If no degradative attack by reaction 2 had occurred or if this degradative attack had removed the chlorine, the same radical would have resulted as from allyl acetate and the conversion would have had to have the same low order. Therefore, the presence of different, more reactive radicals, undoubtedly $-CO\dot{C}HCl$, are indicated. These are capable of starting new chains and are effective carriers, hence consuming more monomer, in contrast to the product from the acetate which is relatively ineffective as far as chain propagation is concerned.

TABLE III

VISCOMETRY IN ALLYL ESTERS

Monomer	Temp., °C.	Time, hr.	Peroxide, moles/ kg.	Polymer, η_{sp}/c	Conversion, %
Allyl acetate[a]	75	4	0.173	0.048[b]	14.7
	15	4	.175	.051[b]	7.9
Allyl chloroacetate[a]	75	5	.0366	.047[b]	15.4
	75	5	.0354	.069[b]	16.9
	15	5	.0354	.037[b]	8.3
	15	4	.0361	.038[b]	7.0
Allyl acetate	80	48	.0845	.047	
	80	48	.204	.048	
	80	48	.411	.037	
Allyl propionate	80	48	.0814	.036	
	80	48	.204	.041	
	80	48	.393	.039	
Allyl trimethylacetate	80	48	.0859	.032	
	80	48	.208	.033	
Allyl ethyl carbonate	80	48	.0836	.047	
	80	48	.204	.046	
	80	48	.370	.059	
Isopropenyl acetate	80	48	.0830	.050	
	80	48	.205	.047	

[a] Data from Cohen, *et al.*,[11] using benzoyl peroxide and ultraviolet light. [b] The polymer was not isolated; η_{sp}/c was determined at 30° from the increase in viscosity of the product and value of per cent. polymer obtained by titration.

Degradative Displacement Reaction.—If the results from the polymerization of allyl trimethylacetate are examined, a striking incongruity is observed. From Table II it is seen that this compound which has no abstractable hydrogen in the acid derived portion of the molecule, and hence only the allylic position available for degradative attack, nevertheless has the lowest $\overline{DP}$ and the smallest dM/dP of all the allyl esters. Either allyl trimethylacetate presents a special case or a new mechanism must be postulated which will account for the behavior of the trimethylacetate within an over-all picture of the allyl esters.

The lowered $\overline{DP}$ at approximately the same conversion is indicative of a greater number of radicals, either from the catalyst, or by effective chain transfer, or may be due to more transfer relative to propagation. The lowered dM/dP may arise by wastage of initiating centers lowering the consumption of monomer per unit center, or may arise from chain transfer to radicals which cannot propagate the chain. From Part II of this series we learn that the decomposition of benzoyl peroxide in the trimethylacetate is more rapid than in the other esters. This may also be indicative of the presence of more radicals assisting in inducing decomposition, *i.e.*, of more transfer to peroxide.

The structure of allyl trimethylacetate reveals the possible origin of a radical which may be an effective carrier, *i.e.*, the trimethylacetate radical. This radical might arise by a free radical displacement on the carbonyl as has been shown to occur in the decomposition of oxalyl chloride, initiated by organic peroxides.[12] However, a more likely reaction would be a displacement at the allylic carbon. Kharasch has shown that in the decomposition of acetyl peroxide in allyl bromide the free methyl radical attacks the allyl bromide, displacing a bromine atom and forming butene. Further, other products isolated in the reaction were postulated as arising in a similar manner.[13] Finally, the induced decomposition of benzoyl or acetyl peroxides has to be considered as a radical displacement reaction which frees acyl radicals. Thus a free radical displacement reaction at the allylic carbon is a likely reaction. The trimethylacetate radical then can arise by a variety of displacement reactions either in the monomer on the allylic carbon or in the polymer on the side chain. It may then decompose to the *t*-butyl radical either spontaneously or at the moment of reaction. In order to include these features in a kinetic scheme leading to the experimentally observed constant

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(11) S. G. Cohen, B. E. Ostberg, D. B. Sparrow and E. R. Blout, *J. Polymer Sci.*, **3**, 264 (1948).

(12) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **64**, 329 (1942).

(13) M. S. Kharasch and G. Buchi, *J. Org. Chem.*, **14**, 84 (1949).

$\mathrm{d}M/\mathrm{d}P$, we can make several changes in the previous scheme.

Replacing allyl acetate by allyl trimethylacetate, equations for k_1, k_a, k_b, k_c, k_2, k_3 and k_5 remain essentially the same. The equations for k_d and k_4 are replaced by the radical displacement reaction

$$\underset{\rho}{C_6H_5COO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOC(CH_3)_3} \xrightarrow{k_d'} \underset{M_1}{CH_2{=}CHCH_2OCOC_6H_5} + \underset{s}{(CH_3)_3CCOO\cdot}$$

$$R + \underset{M}{CH_2{=}CHCH_2OCOC(CH_3)_3} \xrightarrow{k_4'} \underset{M_2}{CH_2{=}CHCH_2R} + \underset{s}{(CH_3)_3CCOO\cdot}$$

Expressions for the disposition of the trimethylacetate radical replace k_6 and k_7.

$$\underset{s}{(CH_3)_3CCOO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOC(CH_3)_3} \xrightarrow{k_{4a}} (CH_3)_3CH + CO_2 + \underset{r}{CH_2{=}CH\underset{\cdot}{C}HOCOC(CH_3)_3}$$

$$\underset{s}{(CH_3)_3CCOO\cdot} + \underset{M}{CH_2{=}CHCH_2OCOC(CH_3)_3} \xrightarrow{k_{4b}} \underset{M_2}{CH_2{=}CHCH_2C(CH_3)_3} + CO_2 + \underset{s}{(CH_3)_3CCOO\cdot}$$

In the steady state

$$-\mathrm{d}M/\mathrm{d}t = (k_a + k_b + k_c)\rho M + (k_2 + k_3)RM + k_{4a}sM$$

$$\mathrm{d}\rho/\mathrm{d}t = 2k_1P - (k_a + k_b + k_c + k_d')\rho M \cong 0$$

$$\rho = \frac{2k_1P}{(k_a + k_b + k_c + k_d')M} = \frac{2k_1P}{k^\circ M} \text{ where } k^\circ = k_a + k_b + k_c + k_d'$$

$$\mathrm{d}R/\mathrm{d}t = (k_a + k_b)\,\rho M - (k_3 + k_4')RM \cong 0$$

$$R = \frac{2k_1P(k_a + k_b)}{k^\circ M(k_3 + k_4')}$$

$$\mathrm{d}s/dt = k_d'\,\rho M + k_4'\,RM - k_{4a}sM \cong 0$$

$$s = \frac{k_d'\rho + k_4'R}{k_{4a}} = \frac{2k_1Pk^*}{k_{4a}k^\circ M} \text{ where } k^* = k_d' + \frac{k_4'(k_a + k_b)}{(k_3 + k_4')}$$

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{2k_1P}{k^\circ}\left[(k_a + k_b + k_c) + \frac{(k_2 + k_3)(k_a + k_b)}{(k_3 + k_4')} + k^*\right]$$

$-\mathrm{d}P/\mathrm{d}t = k_1P$[9]

$$\frac{\mathrm{d}M}{\mathrm{d}P} = \frac{2}{k^\circ}\left[(k_a + k_b + k_c) + \frac{(k_2 + k_3)(k_a + k_b)}{(k_3 + k_4')} + k^*\right] = \text{constant}$$

It should be pointed out that if the following propagation step (chain reinitiation) were included in the kinetic scheme

$$(CH_3)_3CCOO\cdot + M \rightarrow R\cdot$$

the constancy of $\mathrm{d}M/\mathrm{d}P$ would be interfered with. As a matter of fact we have observed that in many cases the data from allyl polymerizations can be fitted as well into a vinyl kinetic scheme. For example, a linear relationship between log M and $\sqrt{P}$ is predicted by vinyl kinetics. This linearity is actually obtained when the appropriate data from the polymerization of allyl trimethylacetate, and for that matter from the other esters, is plotted in this way. It may be concluded that, as already mentioned by Bartlett,[14] effective chain transfer is a regular feature in allyl polymerization although particularly pronounced in allyl trimethylacetate and in allyl chloride. It is apparent that experimental inaccuracies do not permit distinction between two mathematical functions which do not diverge very greatly.[15]

While we believe that with regard to the extent to which radical displacement occurs, allyl trimethylacetate represents a special case, the mechanism as such cannot be excluded for the other allyl esters. The final decision can only come from a careful analysis of reaction products, but the fact that the $\overline{\mathrm{DP}}$ in trimethylacetate is exceptionally low indicates that only in this case do we have an appreciable effective chain transfer from the acid derived portion of the molecule.[16]

Polymerization of Isopropenyl Acetate.—The constancy of the ratio $\mathrm{d}M/\mathrm{d}P$ observed with other allyl esters is equally obtained with isopropenyl acetate (Fig. 2). The similarity of the polymerization of this monomer to that of allyl acetate has been reported.[17] Examination of the constants obtained in the bulk polymerization of this material (Table II) confirms these observations. Further, as pointed out in Part II of this series,[6] the decomposition of benzoyl peroxide in the course of the

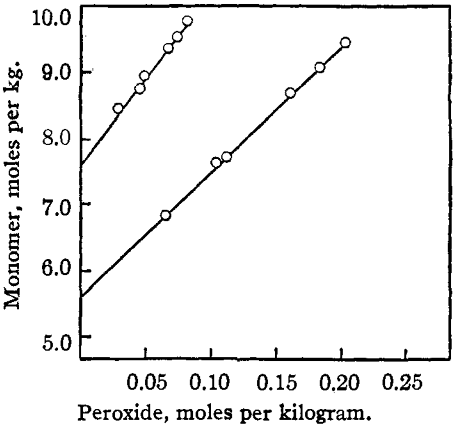

Fig. 2.—Monomer concentration plotted against peroxide concentration in the bulk polymerization of isopropenyl acetate at 80°: upper curve, 2% Bz_2O_2, lower curve, 5% Bz_2O_2. Data from Table I.

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(14) P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 812 (1945).

(15) However, if the disappearance of catalyst is followed to the very end, only the plot $-\mathrm{d}M$ *vs.* $-\mathrm{d}P$ yields straight lines (private communication, P. D. Bartlett).

(16) As stressed by the Referee, an alternative explanation for the kinetics can be given. The order of rate of decomposition of peroxide is trimethylacetate > propionate > acetate > ethyl carbonate. $\overline{\mathrm{DP}}$ and $\mathrm{d}M/\mathrm{d}P$ decrease in the same order from right to left. If chain propagation (k_a and k_2) is more difficult going from right to left in the above monomer series, radicals may react instead with peroxide to induce wastage, increasing $\mathrm{d}P/\mathrm{d}t$ and lowering $\mathrm{d}M/\mathrm{d}P$ with monomers on the left. The necessary trend in k_2 would be that expected from steric effects. Similarly, if propagation becomes more difficult from right to left, but degradative chain transfer (k_b and k_3) is relatively unchanged from monomer to monomer, then $\overline{\mathrm{DP}}$ would be decreased going from right to left. Also, if propagation becomes more difficult, then a transfer reaction with peroxide could become important, giving a lower $\overline{\mathrm{DP}}$ and $\mathrm{d}M/\mathrm{d}P$ and a higher $\mathrm{d}P/\mathrm{d}t$ going from right to left.

(17) R. Hart and G. Smets, *J. Polymer Sci.*, **5**, 55 (1950); N. G. Gaylord and F. R. Eirich, *ibid.*, **5**, 743 (1950).

polymerization of both materials is also similar. Therefore, isopropenyl acetate can be considered as fitting into the same general position in the series of allyl esters as allyl acetate. The reactivity of the double bond would be approximately the same, since Melville and Robb[18] have shown that there is little difference in reactivity whether substituents are on carbon 2 or 3. Primary degradative chain transfer in both compounds is comparable, the increased accessibility and decreased steric hindrance of the side methyl apparently balancing the decreased stability of the primary allylic radical as compared to the secondary allylic radical in allyl acetate.

Experimental

Materials.—The allyl esters and benzoyl peroxide were prepared and purified as described in Part II of this series.[6]

Experimental Procedure.—Polymerizations were carried out as previously described. Samples were removed for determination of unsaturation and peroxide concentration. The analytical methods employed for the allyl esters were similar to those of Bartlett and Altschul.[4] The bromate-bromide solution used was standardized against the allyl monomer under investigation. The concentration of monomer in isopropenyl acetate was determined by removal of residual monomer under vacuum at room temperature to constant weight.

Isolation of Polymer.—The polymer was isolated by removing all volatile material under vacuum at room temperature to constant weight.

Purification of Polymer for Molecular Weight Determinations.—The polymer from the polymerization of the monomer to the exhaustion of peroxide was isolated as above, dissolved in benzene, extracted with aqueous potassium carbonate, dried and isolated as described by Bartlett and Altschul.[4]

Molecular Weight Determinations.—All molecular weights were determined cryoscopically. A solution of the polymer was made up accurately by weight in benzene and transferred to the apparatus for the determination of molecular weights by freezing point depression (Eimer and Amend) utilizing a Beckmann thermometer and mechanical stirring. The values of the freezing point depressions thus obtained were in each case the result of at least two checking determinations.

Viscometric Determinations.—Viscosities were measured in benzene as solvent using a modified Ostwald pipet, in a constant temperature bath operating at 27°.

BROOKLYN 2, N. Y. RECEIVED FEBRUARY 13, 1951

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[18] H. W. Melville and J. C. Robb, *Proc. Royal Soc.* (*London*), **A196**, 494 (1949); *ibid.*, **A202**, 181 (1950).

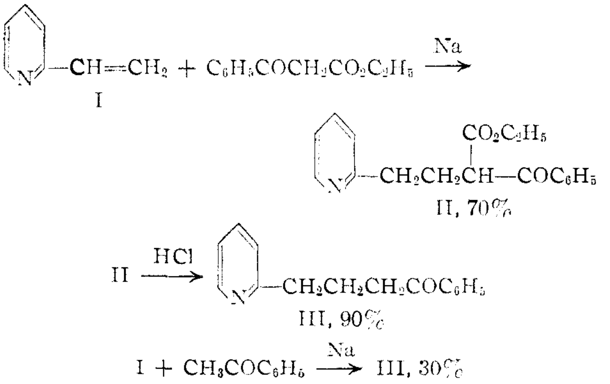
[CONTRIBUTION NO. 829 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Direct Pyridylethylation of Active Hydrogen Compounds. I. 2-Vinylpyridine with Ketones

BY ROBERT LEVINE AND MYRON H. WILT

The Michael condensation has been effected between a number of ketones and 2-vinylpyridine in the presence of sodium metal as the condensing agent. In the pyridylethylation of methyl ethyl ketone and methyl isobutyl ketone, condensation occurs at the α-methylene group of the former and the α-methyl group of the latter compound.

While the ketones, acetone[1] and acetophenone[2] have been pyridylethylated indirectly by the reaction of the sodium derivatives of ethyl acetoacetate and ethyl benzoylacetate with 2-vinylpyridine and subjecting the condensation products to ketonic cleavage, the direct pyridylethylation of the sodium derivatives of these ketones has not been reported previously. The three equations above show how phenyl γ-(2-pyridyl)-propyl ketone may be prepared by these two routes. Since the relatively reactive ketones, phenylacetone and desoxybenzoin, have recently been condensed with 2-vinylpyridine,[3] we are reporting the results we have obtained in similar condensations with a number of other ketones.


I

II, 70%

III, 90%

$$\text{I} + CH_3COC_6H_5 \xrightarrow{\text{Na}} \text{III, } 30\%$$

Most of our condensations have been effected by the interaction of two equivalents of ketone, one equivalent of 2-vinylpyridine and a small amount of sodium metal. The yields and other pertinent data on the compounds we have prepared are found in Table I. It may be seen that acetone has been pyridylethylated in negligible yield. Instead, it has been self-condensed to give a mixture of mesityl oxide and isophorone. The other ketones have been mono-2-pyridylethylated in fair to good yields. Furthermore, it may be seen that in the experiments with methyl ethyl ketone and methyl isobutyl ketone, the respective dehydrated ketols were also formed. In several of the runs, after the monopyridylethylated derivatives were distilled from the reaction mixtures, higher boiling nitrogenous materials were isolated, which probably consist of condensation products of one molecule of the ketone(s) with more than one molecule of vinylpyridine. From the pinacolone run, both mono- and di-2-pyridylethylated products have been iso-

$$CH_3COCH_2CH(CH_3)_2 + 2\text{-}C_5H_4NCH{=}CH_2 \rightarrow \begin{cases} 2\text{-}PyCH_2CH_2CH_2COCH_2CH(CH_3)_2 \quad (\text{IV}) \\ \text{Condensation at the } CH_3 \text{ group} \\ CH_3COCH(CH_2CH_2Py\text{-}2)CH(CH_3)_2 \quad (\text{V}) \\ \text{Condensation at the } CH_2 \text{ group} \end{cases}$$

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[1] Doering and Weil, THIS JOURNAL, **69**, 2461 (1947).

[2] Boekelheide and Agnello, *ibid.*, **72**, 5005 (1950).

[3] Boekelheide and Mason, *ibid.*, **73**, 2356 (1951).