

TABLE IV

RATE DATA FOR THE SECOND-ORDER REACTION OF *t*-AMYL HALIDES WITH POTASSIUM ALKOXIDE IN SEVERAL ALCOHOLS

Methyl alcohol, <i>t</i> -amyl bromide ^a						
Time, hr.	0	1.0	1.33	2.0	2.33	3.0
HCl, ml. ^b	4.423	2.897	2.592	2.170	1.999	1.690
$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹		3.30	3.30	3.25	3.25	3.36
Ethyl alcohol, <i>t</i> -amyl bromide ^a						
Time, hr.	0	1.0	1.67	2.67	3.0	4.0
HCl, ml. ^b	4.133	3.375	3.003	2.582	2.460	2.091
$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹		1.51	1.52	1.51	1.52	1.51
Isopropyl alcohol, <i>t</i> -amyl bromide ^a						
Time, hr.	0	3.0	4.5	5.0	6.0	7.0
HCl, ml. ^b	4.232	3.138	2.772	2.660	2.476	2.308
$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹		0.761	0.767	0.775	0.775	0.769
<i>t</i> -Butyl alcohol, <i>t</i> -amyl bromide ^a						
Time, hr.	0	1.0	2.0	3.0	5.0	7.0
HCl, ml. ^b	3.860	3.682	3.532	3.375	3.133	2.912
$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹		0.347	0.333	0.344	0.333	0.333
<i>t</i> -Butyl alcohol, <i>t</i> -amyl chloride ^a						
Time, hr.	0	24.0	36.0	72.0	85.0	97.0
HCl, ml. ^b	4.537	4.427	4.343	4.235	4.189	4.145
$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹		0.00577	0.00591	0.00586	0.00583	0.00577
<i>t</i> -Butyl alcohol, <i>t</i> -amyl iodide ^a						
Time, hr.	0	0.33	0.67	1.0	1.33	1.5
HCl, ml. ^b	4.438	3.947	3.549	3.231	2.962	2.844
$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹		2.34	2.35	2.34	2.34	2.34

^a Concentrations of *t*-amyl bromide and alkoxides were equal, approximately 1 *M*. ^b 1.145 *N*. ^c Since the quantity of halide which reacts in the presence of base is only slightly greater than the reaction observed in methanol alone, the calculation of k_2 must be meaningless. However, it is of interest that the calculation results in an excellent constancy in the value for k_2 . We have not attempted to explain the reason for this constancy.

of this high concentration were utilized so that the rate data could be directly compared with those obtained for the second-order reaction.) Each reaction mixture of 100 ml. was maintained at 25.0°, 5.0-ml. aliquots removed at convenient time intervals, the reaction halted with cold (0°) absolute ethanol, and the acid formed titrated with 1.032 *N* sodium hydroxide. Typical rate data are summarized in Table III.

Second-Order Reaction.—Sufficient potassium was dissolved in the anhydrous alcohol and *t*-amyl bromide then added to make the solution approximately 1.0 *M* in both the alkoxide and halide. The reaction mixture was main-

tained at 25.0°. At suitable intervals 5.0-ml. aliquots were removed, added to cold (0°) absolute ethanol to halt the reaction, and the extent of reaction followed by titration for residual base. Typical rate data are summarized in Table IV.

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LAFAYETTE, INDIANA

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The Additions of Chloroform and Carbon Tetrachloride to Allylic Monomers¹

By FREDERICK M. LEWIS^{2a} AND FRANK R. MAYO^{2b}

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The benzoyl peroxide-initiated reactions of propylene, isobutylene, allyl acetate and allyl chloride with carbon tetrachloride, and of propylene and isobutylene with chloroform have been studied at 100°. Various monomer-solvent ratios and concentrations of initiator were employed in order to determine how the most addition product per initiator molecule can be obtained, and to distinguish among five possible mechanisms of chain termination. At 0.01 mole % of benzoyl peroxide, 600 moles of addition product could be obtained per mole of peroxide from isobutylene and carbon tetrachloride, only 3 moles from isobutylene and chloroform. Optimum solvent-monomer feed ratios varied from 1 to 10. Nearly all reaction mixtures gave products averaging more than one monomer unit per molecule. From the compositions of these products, the relative reactivity of solvent and monomer toward the radicals $\text{Cl}_3\text{C}-(\text{CH}_2-\overset{\text{R}_1}{\text{C}})_n$ is found to increase at least fivefold as n increases from 1 to 3. Yields are discussed in terms of termination mechanisms, transfer constants and polar and steric effects.

Quantitative relationships in the chain transfer reactions of solvents with readily polymerizable monomers were investigated some time ago and

are fairly well understood.³ When Dr. E. C. Ladd of this Laboratory discovered that some monomers which do not polymerize readily or give only short chains with free radicals nevertheless give good

(1) This experimental work was presented at the Conference on Organic Reaction Mechanisms, University of Notre Dame, September 3-6, 1946.

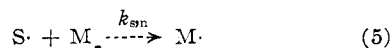
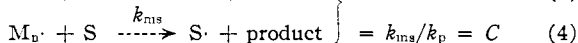
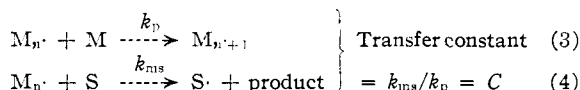
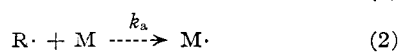
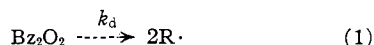
(2) (a) General Electric Co., Waterford, N. Y.; (b) General Electric Research Laboratory, Schenectady, N. Y.

(3) (a) F. R. Mayo, *THIS JOURNAL*, **65**, 2324 (1943); (b) R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948); (c) *Disc. Faraday Soc.*, **2**, 328 (1947); (d) F. R. Mayo, *THIS JOURNAL*, **70**, 3689 (1948); (e) R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948).

yields of chain transfer addition products,⁴ some factors influencing yields were investigated. By analogy with other additions of chloroform and carbon tetrachloride,⁵ these halides (Cl_3CX) add to terminally unsaturated olefins, $\text{H}_2\text{C}=\text{CR}_1\text{R}_2$, by a free radical chain reaction to give products of the structures $\text{Cl}_3\text{C}-(\text{CH}_2-\text{CR}_1\text{R}_2)_n-\text{X}$, where n is usually 1 or 2.

The plan of the present work was to carry out two series of experiments with each monomer-solvent combination, one series at nearly constant concentration of initiator and various monomer-solvent ratios, the other series with various peroxide concentrations near the optimum monomer-solvent ratio. Because this work was planned as a rapid survey, some desirable data are lacking, but it provided the starting point for a quantitative study⁶ of the addition of bromotrichloromethane⁷ to methallyl acetate.

Kinetics of Solvent-Monomer Reactions.—The discussion below assumes that the decomposition of each initiator (benzoyl peroxide) molecule yields two free radicals ($\text{R}\cdot$), both of which add to monomer to give monomer radicals ($\text{M}\cdot$). The latter may add to more monomer, giving another radical, assumed for the present to have the same reactivity, or it may remove an atom from the solvent (S), leaving product and a solvent radical ($\text{S}\cdot$), which may add to monomer. The recent paper by Kooyman and Farenhorst^{8a} has demonstrated that this is a major mechanism of chain initiation although some initial solvent attack also occurs. Actually, the details of initiation are not important for our present purposes. In our terminology, the reaction steps are:



Five mechanisms of chain termination may be expected, two involving monomer radicals, two involving solvent radicals, and one involving one radical of each type. At high enough monomer and low enough solvent concentrations, $[\text{M}\cdot] \gg [\text{S}\cdot]$.

(4) United States Rubber Co., British Patent 638,414; *C. A.*, **44**, 8359 (1950). The first published report of such a reaction is by M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945). In general, the U. S. Patents on additions of aldehydes, *e. g.*, 2,517,684 and 2,533,944, were issued to E. C. Ladd, and those on additions of bromochloromethanes, *e. g.*, 2,468,208, and 2,574,832, were issued to M. S. Kharasch, all being assigned to the United States Rubber Company.

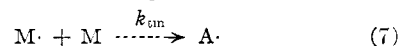
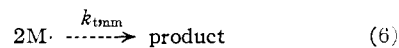
(5) M. S. Kharasch, E. V. Jensen and W. H. Urry, *THIS JOURNAL*, **69**, 1100 (1947); R. M. Joyce, W. E. Hanford and J. Harmon, *ibid.*, **70**, 2539 (1948); J. Harmon, T. A. Ford, W. E. Hanford and R. M. Joyce, *ibid.*, **72**, 2213 (1950).

(6) M. S. Matheson and D. C. Seymour, unpublished work.

(7) M. S. Kharasch, O. Reinmuth and W. H. Urry, *THIS JOURNAL*, **69**, 1105 (1947).

(8) (a) E. C. Kooyman and E. Farenhorst, *Rec. trav. chim.*, **70**, 867 (1951); (b) E. C. Kooyman, *ibid.*, **69**, 492 (1950); (c) E. C. Kooyman, *Disc. Faraday Soc.*, **10**, 163 (1951); (d) discussions by E. C. Kooyman and by H. W. Melville, *et al.*, *ibid.*, **10**, 224 (1951).

Kinetic chains must then end by reactions which remove $\text{M}\cdot$.



where $\text{A}\cdot$ represents an unreactive allyl radical which is assumed to react with another $\text{M}\cdot$ (two radicals and two kinetic chains being destroyed as a result of one reaction 7.^{9,10} Termination mechanisms 6 and 7 lead, respectively, to the relations

$$d[\text{S}]/d[\text{Bz}_2\text{O}_2] = k_{ms}[\text{S}]/(k_d k_{tm})^{1/2} [\text{Bz}_2\text{O}_2]^{1/2} \quad (6a)$$

$$d[\text{S}]/d[\text{Bz}_2\text{O}_2] = k_{ms}[\text{S}]/k_{tm}[\text{M}] \quad (7a)$$

between solvent consumption (equal to rate of product formation in moles) and peroxide consumption. Under conditions where a substantial proportion of peroxide or solvent reacts, these equations become

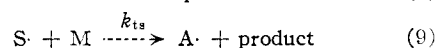
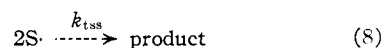
$$\ln(S_0/S) = 2k_{ms}([\text{Bz}_2\text{O}_2]_0^{1/2} - [\text{Bz}_2\text{O}_2]^{1/2})/(k_d k_{tm})^{1/2} \quad (6b)$$

$$\ln(S_0/S) = k_{ms}([\text{Bz}_2\text{O}_2]_0 - [\text{Bz}_2\text{O}_2])/k_{tm}[\text{M}] \quad (7b)$$

where $[\text{M}]$ is taken as constant at its average value. When either equation applies, the moles of product formed, for a given amount of initiator decomposed, increase as the solvent:monomer ratio increases, because each monomer radical will have a better opportunity to transfer with the solvent before the radical is destroyed.

The section on effect of chain length will show that k_{ms} is not constant, but that it may probably be made so in a series of experiments by dividing it by the average transfer constant, C_{av} , in each experiment.

At the other extreme, at high enough solvent and low enough monomer concentrations, $\text{S}\cdot$ must accumulate and disappear by



After 9, $\text{A}\cdot$ is assumed to react with $\text{S}\cdot$ (two radicals and two kinetic chains being thus destroyed). These mechanisms lead to the relations

$$d[\text{S}]/d[\text{Bz}_2\text{O}_2] = k_{sm}[\text{M}]/(k_d k_{ts})^{1/2} [\text{Bz}_2\text{O}_2]^{1/2} + 2 \quad (8a)$$

$$d[\text{S}]/d[\text{Bz}_2\text{O}_2] = k_{sm}/k_{ts} + 2 \quad (9a)$$

The 2's arise from the postulated mechanism which requires that at least two solvent molecules react for each benzoyl peroxide molecule decomposing. The term is of little significance, since the chains are usually much longer, and will be neglected. The integrated forms of 8a and 9a are

$$\ln \frac{M_0}{M} - \frac{1}{C_{av}} \ln \frac{S_0}{S} = \frac{2k_{sm}([\text{Bz}_2\text{O}_2]_0^{1/2} - [\text{Bz}_2\text{O}_2]^{1/2})}{(k_d k_{ts})^{1/2}} \quad (8b)$$

$$[\text{S}]_0 - [\text{S}] = k_{sm}([\text{Bz}_2\text{O}_2]_0 - [\text{Bz}_2\text{O}_2])/k_{ts} \quad (9b)$$

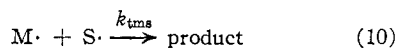
When reaction 8 applies, the yield of product

(9) P. D. Bartlett and R. Altschul, *THIS JOURNAL*, **67**, 812, 816 (1945); P. D. Bartlett and F. A. Tate, *ibid.*, **75**, 91 (1953).

(10) If instead, $2\text{A}\cdot \rightarrow \text{product}$, eq. 7a becomes $d[\text{S}]/d[\text{Bz}_2\text{O}_2] = 2k_{ms}[\text{S}]/k_{tm}[\text{M}]$ and eq. 9a becomes $d[\text{S}]/d[\text{Bz}_2\text{O}_2] = 2k_{sm}/k_{ts} (+2)$, but the factors of 2 do not affect our argument. Corresponding factors will appear in 7b and 9b. Kooyman and Farenhorst^{8a} have established the latter termination mechanism in the cyclohexane-carbon tetrachloride-benzoyl peroxide reaction by isolating good yields of chloroform and dicyclohexenyl, but they have been unable to find corresponding coupling or disproportionation products from the more reactive 1-alkenes.

increases with the concentration of monomer (which permits growth of kinetic chains which would otherwise die). When reaction 9 applies, the yield per unit catalyst becomes independent of [S] and [M], both termination and propagation steps involving different reactions of the same reactants. As the monomer concentration vanishes, this reaction 9 must necessarily be superseded by reaction 8.

Between these extremes, there must be a range where termination involves both M· and S·, and our knowledge of crossed termination reactions,¹¹ recently confirmed by Melville, Robb and Tutton,¹² suggests that reaction 10 should be favored over both reactions 6 and 8 when appreciable quantities of both hydrocarbon radicals and trichloromethyl radicals are present.



Taking the rate of disappearance of radicals^{11b} by 10 as

$$4k_{tms}[M\cdot][S\cdot]$$

this mechanism leads to the relation

$$d[S]/d[Bz_2O_2] = 1/2 \left(1 + \sqrt{\frac{1 + 2k_{ms}[S]k_{am}[M]}{k_d[Bz_2O_2]k_{tms}}} \right) \quad (10a)$$

The form of this equation will be the same if M· represents an allyl as well as an alkyl radical, providing that allyl radicals are capable of continuing the reaction chains. The integrated form of this equation is too complicated to be useful, but inspection shows that when this termination mechanism alone applies, then the highest yields per unit peroxide should be obtained at approximately equal concentrations of M and S (where their product is largest), and at low peroxide concentrations. The yield per unit initiator with this mechanism will be proportional to $[Bz_2O_2]^{-1/2}$ for long chains, and become independent of initiator for very short chains. Practically, however, other termination mechanisms complicate the situation.

Experimental

Reactions were carried out in heavy-walled Pyrex tubes. Recrystallized benzoyl peroxide was added as a solution in the solvent employed and additional solvent was weighed out to 0.1 g. Allyl acetate and allyl chloride were weighed out similarly. Cooled liquid isobutylene and propylene were added from a cooled hypodermic syringe and weighed with an accuracy of 0.1 g. for large charges, 0.01 g. for charges under 2 g. The tubes were filled with nitrogen, sealed off and heated 16–18 hours at 100° to complete decomposition of the peroxide. After the reaction tubes were cooled and opened, the reaction mixtures were concentrated by distillation to a volume of about 15 ml. This residue was then distilled at atmospheric pressure from a 25-ml. flask under a 10-cm. column packed with glass helices. The distillation was stopped when a thermocouple at the top showed that all the monomer and solvent had distilled. The column and flask were then weighed to obtain the weight of reaction product. Test on a known mixture showed that this procedure was accurate to 1%.

The volumes of the reaction mixtures were not measured but are needed for calculations of $[Bz_2O_2]_0^{1/2}$ in testing equa-

(11) (a) C. Walling, *THIS JOURNAL*, **70**, 2561 (1948); (b) *ibid.*, **71**, 1930 (1949); (c) H. W. Melville and L. Valentine, *Proc. Roy. Soc. (London)*, **200**, 337, 358 (1950); (d) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(12) H. W. Melville, J. C. Robb and R. C. Tutton, *Disc. Faraday Soc.*, **14**, 150 (1953).

tions 6b and 8b. All other quantities of reactants appear as ratios so that directly measured quantities instead of calculated concentrations can be used. The volumes appearing in the tables have been estimated from densities in the literature, assuming no volume change on mixing of liquid monomer and solvent. The volume change on mixing methyl acetate and bromotrichloromethane is only 0.1%⁶; considering the limited use of volume estimates, errors from this source are unimportant.

Effect of Temperature.—With two systems, series of experiments were carried out at both 80 and 100° at the same initial monomer-solvent-initiator ratios, following the yield and peroxide concentrations as functions of time. The decomposition of benzoyl peroxide was essentially first order in every case.

With 0.137 mole of isobutylene, 0.41 mole of carbon tetrachloride, and 0.000418 mole of peroxide, k_d for the peroxide was 0.09 hr.⁻¹ at 80°, 1.0 hr.⁻¹ at 100°, nearly the same as in benzene. The yield-peroxide relation corresponded with a bimolecular termination mechanism. Of the three possible mechanisms, 6, 8 and 10, the latter is preferred, because the feed ratio was in the transition region, as in expt. 4A–E in Table II.

With 0.082 mole of allyl acetate, 0.41 mole of carbon tetrachloride, and 0.000413 mole of peroxide, k_d for the peroxide was 0.104 hr.⁻¹ at 80°, 0.933 hr.⁻¹ at 100°. The yield-peroxide relations agreed well with those expected from termination by interaction of two solvent radicals (equation 8b), as found in experiments 3A–E in Table II.

With both systems, yields per initiator molecule decomposed were about twice as high at 80° as at 100°. Because the peroxide decomposes only one-tenth as fast at the lower temperature, it is used more effectively in reactions with second-order terminations.

Effect of Chain Length in Reaction of Radicals with Solvents.—The only solvents considered in this paper are chloroform, Cl_3C-H , and carbon tetrachloride, Cl_3C-Cl , which add as indicated in the introduction. The developments of the last section assumed that the rate constants for the reactions of "monomer radicals," $Cl_3C-(M)_n$, are independent of n (but of course depend on M). The only quantitative information known to us, where M is styrene^{3d} or ethylene,^{13b} proves that the ratio, k_{ms}/k_p , varies with n in chain transfer reactions with carbon tetrachloride and chloroform, and indicates that the change is due mostly or entirely to changes in k_{ms} , the rate constants, k_p and k_{tmm} , being independent of n . In the absence of other information, the same relations will be assumed to apply here. Since this paper is concerned principally with products averaging 1–3 monomer units, and since the relations 6a, 6b, 7a and 7b therefore involve k_{ms} in the range where it is sensitive to n , calculations of the effect of chain length on the ratio, k_{ms}/k_p , will be considered first; they are summarized in Table I.¹⁴ In the Table, the ratio, k_{ms}/k_p , is assumed to remain constant above $n = 1$, or above $n = 2$, depending on the adequacy of the data. The constant ratio is the transfer constant,^{3a} C , and the ratios for short radicals are designated C_1 and C_2 . Accurate determinations are often impossible from the data, and the errors are only

(13) (a) J. R. Little, L. W. Hartzel, F. O. Guenther and F. R. Mayo, *THIS JOURNAL*, paper in preparation; (b) J. R. Little, C. H. Stiteler, F. O. Guenther, F. R. Mayo, H. Sargent and M. P. Harvey, paper in preparation. Qualitative indications of such a change with allyl chloride and carbon tetrachloride have been found by Kharasch, *et al.*⁷

(14) Calculations are based on equations 21 and 22 in ref. 3d. Equation 22 for C_1 and C is readily solved graphically, a plot of C_1 against $1/C$ giving a straight line for each experiment. Equation 21 requires three experiments to solve for C_1 , C_2 and C , but if C_1 is known well enough from equation 22, C_2 and C are readily determined graphically by plotting C_2 against $1/C$.

TABLE I
 VARIATION IN TRANSFER CONSTANT (k_{ms}/k_p) WITH n IN $Cl_3C-(CH_2-CRR')_n$.

System	k_{ms}/k_p assumed constant beyond					
	$n = 1$		$n = 2$		C^b	
	C_i	C^a	C_i	C_i	C_i	C^b
Isobutylene- CCl_4	1.4 ± 0.4	17 ± 3				
Propylene- CCl_4	$1 \pm .3^c$	5-10				
Propylene- $CHCl_3$	$0.1 \pm .02$	0.8 ± 0.1	0.11 ± 0.01	0.55 ± 0.03	1.03 ± 0.05	
Allyl chloride- CCl_4	$.01 \pm .01$	$.28 \pm .05$.01 to .02	$.10 \pm .05$	$0.48 \pm .03$	
Allyl acetate- CCl_4	$.01 \pm .01$	$1.2 \pm .4$	$.01 \pm .01$	$.5 \pm .2$	2.0 ± 1.0	

^{a,b} Calculated from data in Table II on the assumption that k_{ms}/k_p is constant beyond (a) one, or (b) two, monomer units in the radical. The (a) value is seen to be a compromise between C_2 and the (b) value. ^c The data of Kooyman and Fahrenhorst^{8a} indicate that C_1 for propylene and cetene at 90-95° are about 1.6 and 1.4, respectively.

estimates, but in the propylene-chloroform set, four experiments gave remarkably consistent results for three unknowns. Table I shows that in every case the radical with a Cl_3C group and one monomer unit is much less reactive in transfer than the longer units, and that the decreased transfer reactivity is still significant for the radical with two monomer units.

In the experiments which follow, the mean effective transfer constant, C_{av} , has been calculated in each experiment from the relation, $\Delta M/\Delta S = ([M]/C_{av}[S]) + 1$. Since available data with styrene and carbon tetrachloride^{8a} indicate that k_p , or at least the ratio $k_p/k_{tmm}^{1/2}$, is independent of chain length, the experimental quantity, k_{ms}/k_p (C_{av}) has been substituted for k_{ms} in tests of equations (6) and (7), thus permitting correction of the effect of chain length on k_{ms} . While this correction may be inadequate, it is probably much better than none.

Determination of Mechanism of Chain Termination.—This section will describe the method used to determine the mechanism of chain termination. The results are not clear-cut, partly because of insufficient data, and partly because two or more termination mechanisms operate simultaneously. However, the latter complication also arises in polymerization of allylic monomers.

In general, in high monomer feeds, chains must end by reactions 6 or 7 and the amount of solvent reacting will increase as solvent is added. In high solvent feeds, chains must end by reactions 8 or 9 and, at least at the extreme high solvent range, the amount of solvent reacting must increase as monomer is added. Maximum conversion of solvent will be obtained when the termination mechanism changes from 6 or 7 to 8 or 9, probably at least partly through reaction 10. In this transition region, where experiments at constant monomer-solvent ratios and various initial peroxide concentrations were carried out, the data gave no indication of what radicals are involved in termination, but they do indicate whether one (equations 7 and 9) or two (equations 6, 8 and 10) radicals are involved in the termination mechanism.

For the experiments in Table II, reaction mixtures were heated to complete decomposition of benzoyl peroxide, simplifying tests of equations 6b, 7b, 8b and 9b. At least two series of experiments were run with each monomer-solvent combination. In experiments designated by numbers, the monomer-solvent ratio was changed at nearly constant peroxide concentration. When these runs

cover wide enough concentration ranges outside of the transition region, a distinction between the two termination mechanisms on each side of the transition region is possible. In experiments designated by letters, the initial peroxide concentration was varied at constant monomer-solvent ratio, usually at or near the transition region. These experiments have proved less fruitful in bringing out differences between combinations, partly because of the possibility of the crossed bimolecular termination mechanism 10, but also because they show that termination reactions which are first and second order in radicals usually appear together in allylic systems.

The same situation occurs in peroxide-catalyzed polymerizations of allyl chloride without solvent, both in the work of Bartlett, *et al.*,⁹ at 80°, and in the present work at 100° (expt. A and B with allyl chloride, B and C with allyl acetate in Table II). As the initial concentration of peroxide increases, the number of monomer molecules polymerizing per peroxide molecule decomposed falls off according to the relation $\Delta M/\Delta Bz_2O_2 \sim 1/[Bz_2O_2]^n$, where n is between 0 and $1/2$. Although our experiments employed lower peroxide concentrations than those of Bartlett, *et al.*, our higher temperature results in faster decomposition and less efficient utilization of peroxide (see section on Effect of Temperature), offsetting the usually favorable effect of dilution.

Bartlett and Tate⁹ have proposed reasonable explanations for the falling off of $\Delta M/\Delta Bz_2O_2$ at higher peroxide concentrations: at low radical concentrations, the unreactive allyl radicals have a longer life to add to allyl acetate before meeting another radical; at higher peroxide concentrations, more peroxide is wasted by chain transfer of polymer radicals with peroxide. The practical result is that in polymerization as well as in monomer-solvent reactions, experiments at various peroxide concentrations are apt to exhibit results intermediate between those anticipated for first- and second-order termination mechanisms. The most clear-cut characteristic of the degradative chain transfer termination mechanism in polymerization is the constant $\Delta M/\Delta Bz_2O_2$ in a single experiment, although why this ratio remains constant over wide changes in peroxide concentration is an unsolved problem. However, this characteristic may permit experiments at constant peroxide concentration and various monomer-solvent ratios to differentiate between termination mechanisms.

Monomer-solvent systems will now be con-

TABLE II
 REACTION OF CHLOROFORM AND CARBON TETRACHLORIDE WITH UNSATURATED COMPOUNDS AT 100°^{aa}

Expt.	M_0 , moles	S_0 , moles	Bz_2O_2 , moles $\times 10^3$	Product G.	Cl, %	Vol. at 100°, ^b ml.	$\frac{M}{S_{av}}$	$-\Delta M$, moles	$-\Delta S$, moles	$\frac{\Delta M}{\Delta S}$	C_{av}	$[Bz_2O_2]$, moles/l. $\times 10^4$	Eq. 6b (2M) ^c	Eq. 7b ($\frac{M^*}{M}$) ^d	Eq. 8b (2S) ^e	Eq. 9b ($\frac{S^*}{M}$) ^f
A. Isobutylene and Carbon Tetrachloride																
1	0.400	0.0513	2.06	0.416	50.7	50.4	7.89	0.00334	0.00149	2.25	6.3	4.09	0.10	39	0.080	72
2	.205	.205	2.06	1.702	61.4	44.9	0.995	.0100	.00739	1.36	2.8	4.59	.27	55	.75	357
3	.137	.41	2.06	3.101		59.2	.320	.0167	.0141	1.19 ^h	1.69	3.48	.42	56	2.5	680
4C	.0585	.41	2.06	3.270	65.8	50.4	.125	.0166	.0152	1.09	1.42	4.09	.57	28	6.6	738
5	.0316	.41	2.06	2.730		47.3	.062	.0134	.0129	1.04 ^h	1.46	4.36	.46	12	11	624
6	.0205	.41	2.06	2.581	67.0	46.1	.035	.01255	.0122	1.03	1.17	4.47	.54	7.7	19	592
4A	.0585	.41	0	0.666	69.7	50.4	.139	.00317	.00317	1.0						
4B	.0585	.41	0.83	2.136	66.3	50.4	.131	.0107	.00998	1.07	1.87	1.65	.45	36	6.4	832
4D	.0585	.41	4.13	4.966		50.4	.116	.0231	.0249	1.08 ^h	1.50	8.19	.60	19	7.1	605
4E	.0585	.41	8.26	7.180	66.3	50.4	.103	.0336	.0360	1.07	1.47	16.4	.67	13	8.5	435
B. Propylene and Carbon Tetrachloride																
1	0.205	0.205	4.13	1.352	64.19	43.5	0.990	0.00976	0.00611	1.60	1.65	9.49	0.25	38	0.43	148
3	.137	.41	4.13	2.229	68.55	58.2	.321	.01361	.0108	1.29	1.11	7.09	.39	33	1.33	261
4C	.082	.41	4.13	1.444	69.03	52.4	.192	.00863	.00703	1.23	0.84	7.88	.32	17	1.40	170
5	.041	.41	4.13	0.768	69.05	48.1	.0956	.00459	.00374	1.23	.41	8.58	.34	9.3	1.43	91
6	.0205	.41	4.13	.369		46.0	.048	.00195	.00186	1.05 ⁱ	1.00	8.98	.66	0.93	1.39	45
4A	.082	.41	0.83	.520		52.4	.197	.00300	.00256	1.17 ⁱ	1.15	1.58	.19	23	1.10	309
4B	.082	.41	2.06	0.933		52.4	.194	.00538	.00459	1.17 ⁱ	1.14	3.93	.22	16.5	1.28	223
4D	.082	.41	8.26	2.943		52.4	.183	.0169	.0145	1.16 ⁱ	1.11	15.8	.35	13	2.17	175
4E	.082	.41	16.52	5.780	70.66	52.4	.167	.0321	.0283	1.13	1.25	31.5	.44	9.9	3.41	171
2A	.205	.41	0.83	0.765		65.4	.497	.00489	.00361	1.37 ⁱ	1.36	1.27	.27	69	.77	435
2B	.205	.41	2.07	1.470		65.4	.492	.00949	.00696	1.36 ⁱ	1.36	3.17	.31	53	.85	335
2C	.205	.41	4.13	2.339		65.4	.488	.0151	.0102	1.36 ⁱ	1.36	6.31	.32	40	1.01	246
2D	.205	.41	8.26	3.684		65.4	.482	.0237	.0175	1.36 ⁱ	1.36	12.63	.39	32	1.12	211
2E	.205	.41	16.52	6.761		65.4	.465	.0433	.0321	1.35 ⁱ	1.33	25.3	.53	29	1.52	194
C. Propylene and Chloroform																
1	0.400	0.400	41.3	1.982	43.2 ⁿ	78.0	0.98	0.0243	0.00805	3.01	0.486	53.0	0.25	17.1	0.121	19
2	.200	.600	41.3	3.003	51.5 ⁿ	75.0	.312	.0301	.01454	2.07	.292	55.1	.49	16.4	.47	35
3C	.120	.600	41.3	3.695	54.55 ⁿ	66.6	.174	.0340	.01896	1.79	.219	62.0	.80	15.8	1.03	46
4	.060	.600	41.3	3.879	58.85 ⁿ	60.3	.075	.0313	.02146	1.46	.165	68.5	1.15	10.3	2.69	52
5	.030	.600	41.3	3.988	60.00 ⁿ	57.2	.027	.0310 ^m	.02249	1.39		72.2				54
3A	.120	.600	10.3	1.033		66.6	.193	.00960	.00528	1.82 ^j	.235	15.5	.42	18.2	.50	51
3B	.120	.600	20.6	2.087		66.6	.186	.01920	.01070	1.80 ^j	.233	30.9	.60	19.3	.75	52
3D	.120	.600	62.0	5.703		66.6	.161	.0518	.0295	1.75 ^j	.216	93.1	1.06	15.4	1.50	48
3E	.120	.600	82.5	7.628		66.6	.154	.0605	.0351	1.73 ^j	.213	124	1.11	13.4	1.64	43
3F	.120	.600	124.0	9.468		66.6	.136	.0835	.0499	1.58 ^j	.204	186	1.37	11.8	2.42	40
D. Allyl Chloride and Carbon Tetrachloride																
1	0.205	0.205	8.27	1.998	59.97	40.7	0.963	0.01835	0.00386	4.75	0.257	20.3	0.79	75	0.19	47
2	.137	.41	8.27	1.834	63.65	56.4	.318	.01493	.00450	3.32	.137	14.66	.91	56	.39	54
3C	.082	.41	8.27	1.242		51.3	.190	.00908	.00356	2.55 ^k	.123	16.12	.77	29	.51	43
4	.041	.41	8.27	1.029	67.12	47.6	.0913	.00736	.00303	2.43	.064	17.37	1.20	23	.85	37
3A	.082	.41	2.07	0.757		51.3	.194	.00555	.00216	2.57 ^k	.124	4.04	.92	70	.60	104
3B	.082	.41	4.14	.958		51.3	.192	.00703	.00275	2.56 ^k	.123	8.07	.83	45	.54	66
3D	.082	.41	16.54	1.952		51.3	.185	.01421	.00562	2.53 ^k	.121	32.2	.87	22	.58	34
3E	.082	.41	33.08	3.491		51.3	.171	.0252	.01016	2.48 ^k	.116	64.5	1.15	19	.81	31
A	.410	.00	8.27	1.014		37.6		.01325 ^o				22.0				
B	.358	.00	161	8.06		32.7		.1053 ^p				491				
E. Allyl Acetate and Carbon Tetrachloride																
1	0.205	0.205	4.13	0.749	31.14	47.0	0.992	0.00495	0.001643	3.01	0.329	8.79	0.36	52	0.274 ^q	39.8
2	.137	.41	4.13	.506	35.73	60.5	.331	.00310	.001275	2.43	.136	6.82	.38	33	.361 ^q	30.9
3C	.082	.41	4.13	.317	36.67	53.8	.198	.00191	.000820	2.33	.085	7.67	.36	20	.363 ^q	19.8
4	.0205	.41	4.13	.097		46.3	.049	.000532	.000285	1.87 ^t	.026	8.92	.36	5.2	.475 ^q	6.9
3A	.082	.41	1.03	.181		53.8	.200	.00105	.00049	2.14 ^t	.093	1.91	.40	44	.437 ^q	47.7
3B	.082	.41	2.06	.247		53.8	.199	.00143	.00067	2.14 ^t	.093	3.83	.39	30	.423 ^q	32.6
3D	.082	.41	8.37	.433		53.8	.197	.00250	.00117	2.14 ^t	.092	15.6	.34	13	.367 ^q	14.0
3E	.082	.41	16.50	.801		53.8	.195	.00463	.00217	2.15 ^t	.091	30.7	.36	12	.493 ^q	13.2
A	.299	.00	0.0	.04				.0004								
B	.410	.00	8.27	.678		50.5		.00677 ^u				16.4				
C	.410	.00	82.7	3.01		50.5		.0300 ^v				164				

^a M_0 , S_0 and Bz_2O_2 represent initial quantities of reagents in moles. $[Bz_2O_2]$ indicates initial concentration in moles/l. at 100°. ^b Densities at 100° in g./cc. measured or estimated: carbon tetrachloride, 1.434, S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910); chloroform, 1.33, C. P. Smyth and S. O. Morgan, *This Journal*, **50**, 1547 (1928); isobutylene, 0.50, C. C. Coffin and O. Maass, *ibid.*, **50**, 1433 (1928); propylene, 0.4, C. A. Winkler and O. Maass, *Can. J. Research*, **9**, 610 (1933); allyl chloride, 0.835, proportional to density of allyl acetate; allyl acetate, 0.82, R. Schiff, *Ann.*, **220**, 71 (1883). ^{c-f} Chain terminating steps indicated by constancy of functions below: ^e $\log(S_0/S)/C_{av}[Bz_2O_2]^{1/2}$, ^d $M \log(S_0/S)/C_{av} Bz_2O_2$, ^f $[\log(M_0/M) - \log(S_0/S)]/C_{av}[Bz_2O_2]^{1/2}$, ^f $-\Delta S/Bz_2O_2$. Note that k_{ms} in the functions corresponding to 6b and 7b have been replaced by C_{av} to correct for the effect of chain length. ^g Equation 8b cannot be applied accurately because conversions are so low; eq. 8a has therefore been integrated taking $[M]$ as constant at its average value to give $[S]_0 - [S] = 2k_{sm} [M] ([Bz_2O_2]_0^{1/2} - [Bz_2O_2]^{1/2}) / (k_d k_{ts})^{1/2}$. The function tested is $-\Delta S/M[Bz_2O_2]^{1/2}$. ^{h-i} Where chlorine analyses are not available, product compositions are calculated on the bases that C_1 and C_2 , respectively, are ^h 1.4 and 17, ⁱ 1 and 5, ^j 0.1 and 0.8, ^k 0.01 and 0.3, ^l 0.02 and 1.0. ^m Corresponds to 103% reaction of propylene. ⁿ Mean of duplicate analyses. ^{o-v} $\Delta M/Bz_2O_2 = ^o$ 160, ^p 63.5, ^q 82, ^r 36.

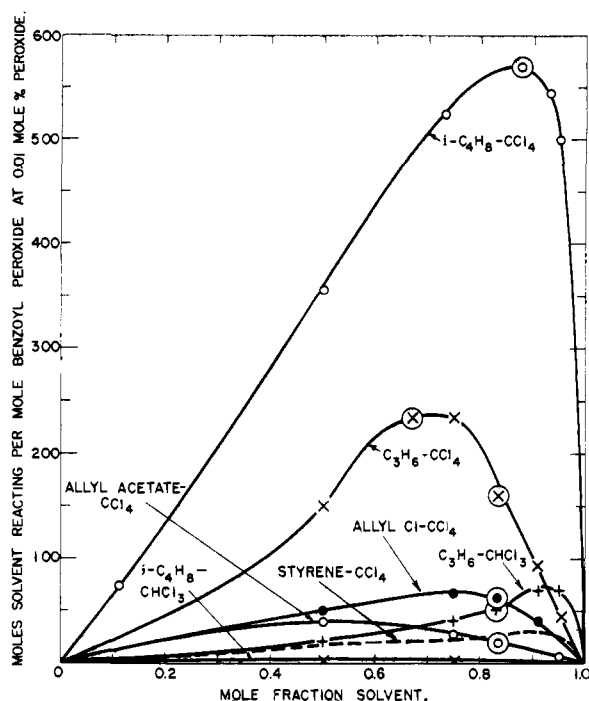


Fig. 1.—Yields of addition products from various monomer-solvent concentrations at 100°. Large circles indicate feeds where peroxide concentration was varied.

sidered. Figure 1, to be discussed later, indicates the relations of various experiments to the transition regions. Table II shows that in the high monomer range of the isobutylene-carbon tetrachloride and propylene-chloroform systems, equation 7b provides a better correlation than equation 6b and therefore that chains end mostly by degradative chain transfer (reaction 7). This conclusion on the chloroform-propylene system is confirmed by expt. 3A-E with various peroxide concentrations. These results mean that the allyl radicals involved do not readily react with either monomer or solvent. Data are inadequate for other solvent-high monomer combinations.

In high carbon tetrachloride feeds with propylene and allyl acetate, experiments at both varied monomer-solvent ratios and peroxide concentrations point to termination by two trichloromethyl radicals (reaction 8), although there is a marked tendency toward degradative chain transfer (reaction 9) with propylene at high peroxide concentrations. Data with other systems are inadequate. Kooyman, *et al.*, have investigated carefully some reactions of a moderate excess carbon tetrachloride with 1-alkenes. With cetene at 91.5°, the bound halogen is directly proportional to the benzoyl peroxide decomposed.^{3c} Since they used relatively high proportions of peroxide, this result supports our conclusion with propylene. The importance of allylic hydrogen atoms in the termination reaction is brought out by their experiments with *t*-butylethylene, which has no such hydrogen atom. This alkene required only 5–10% as much peroxide for the same conversion, and a trace of hexachloroethane (not found in other systems) was identified.^{8a,b}

In all three series with various peroxide concen-

trations in the transition region, results are intermediate between those expected for first and second order termination mechanisms, as judged by the constancy of the functions for equations 6b and 8b or for 7b and 9b. Participation in termination of mechanism 10 cannot be determined directly, since it can result in either extreme in termination mechanism, or something in between. In reactions of carbon tetrachloride with isobutylene, termination is closer to bimolecular. With carbon tetrachloride and propylene or allyl chloride, termination in the transition region tends to approach second order at low peroxide concentrations, first order at high peroxide concentrations. This result means that at low total radical concentrations, most of the (substituted) allyl radicals continue reaction chains; at high total radical concentrations, they react with other radicals.

Isobutylene and chloroform gave such low yields of reaction product that no further analysis was attempted. Results are summarized in Table III.

TABLE III

THE REACTION OF ISOBUTYLENE AND CHLOROFORM AT 100° IN PRESENCE OF 0.1 G. (0.00041 MOLE) OF BENZOYL PEROXIDE

Initial reactants CHCl ₃ , moles	<i>i</i> -C ₄ H ₈ , moles	S ₀ /M ₀	G.	Product, Moles ^a
0.3	0.10	3	0.201	0.00114
.4	.04	10	.242	.00138

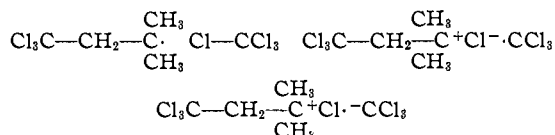
^a Assuming $\Delta M/\Delta S = 1$.

Yields in Monomer-Solvent Reactions.—Figure 1 summarizes our studies of six systems, giving the number of moles of *solvent* reacting per mole of benzoyl peroxide decomposed when all of an initial 0.01 mole % of peroxide (on monomer plus solvent) decomposes at 100°. Actual yields, at lower peroxide concentrations, were often higher and a few points in the figure are based on guesses about the relative contributions of first- and second-order termination reactions. The maximum in each curve must correspond to a change in termination mechanism. The monomer-solvent ratios in the products at these maxima vary from 1:1 for isobutylene-carbon tetrachloride to about 3 with allyl acetate and allyl chloride. In every case, similar plots of moles of *monomer* reacting would lie above those shown by the factors $\Delta M/\Delta S$ shown in the tables. The smallest difference between monomer and solvent consumption is found with isobutylene and carbon tetrachloride. Here, the formation of 1:1 addition product is clearly responsible for the high consumption of both monomer and solvent, and consumption of both approaches zero in the absence of solvent. The largest difference in monomer and solvent consumption is found with allyl chloride and carbon tetrachloride, 222 molecules of monomer reacting per peroxide molecule in expt. 1 at 50 mole % of solvent. Here, however, in the absence of solvent at nearly the same peroxide concentration (expt. A), nearly as much monomer, 160 molecules, reacts per molecule of peroxide.

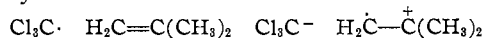
Three factors can be recognized in the ability of certain solvents to increase the number of moles of

monomer reacting per mole of peroxide. The first factor, a change in termination mechanism, is brought out better by results of others. In the reaction of carbon tetrachloride with cyclohexene, both Kooyman and Farenhorst^{8a} and Israelashvili and Shabatay¹⁵ obtained some 3-chlorocyclohexene, demonstrating that some cyclohexenyl radicals were able to react with solvent and continue reaction chains. When the solvent is sufficiently reactive, apparently all the (substituted) allyl radicals continue reaction chains: with bromotrichloromethane, the termination reaction is second order in radicals over the whole range studied with both methallyl acetate⁶ and cyclohexene,¹² but first order with cyclohexene and carbon tetrachloride.^{8a}

A second factor which increases monomer consumption in some combinations is a polar effect. This factor is best illustrated by isobutylene and carbon tetrachloride, which give by far the most reaction product and most nearly a 1:1 reaction product of the systems considered here. The polar factor is most important when contributions of additional ionic resonance structures to the transition state would be expected to be most important,¹⁶ and promotes both steps in the chain process, the reaction of the isobutylene radical with carbon tetrachloride



and the reaction of the trichloromethyl radical with isobutylene



The relatively high stability of tertiary carbonium ions accounts for the high reactivity of isobutylene as compared with other monomers in Table II, and the contributions of chloride ion to the transition states with carbon tetrachloride may explain its higher reactivity as compared with chloroform (where hydrogen is transferred). The steeply rising curve for isobutylene and carbon tetrachloride at both sides of Fig. 1 is thus accounted for.

Table IV shows the relative reactivities of carbon tetrachloride and chloroform toward a series of radicals. The trend strongly suggests that reaction with carbon tetrachloride is most favored with the radicals which are the best electron donors.¹⁷ The polar effect accounts also for the increase in transfer constant with chain length in Table I: the closer is the trichloromethyl group to the free

(15) S. Israelashvili and J. Shabatay, *J. Chem. Soc.*, 3261 (1951).

(16) C. Walling, D. C. Seymour and K. B. Wolfstirn, *THIS JOURNAL*, **70**, 2559 (1949); C. Walling, *ibid.*, **70**, 2561 (1949); F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); F. R. Mayo, *Disc. Faraday Soc.*, **14**, 254 (1953). See also E. C. Kooyman, R. van Helden and A. F. Bickel, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **56B**, 75 (1953).

(17) The inversion of the relative reactivities of the two solvents with the radicals from acetyl peroxide suggests that this peroxide yields acetoxy rather than methyl radicals. If the peroxide yields methyl radicals, the sequence corresponds both to increasing size and decreasing reactivity of the radicals, but the difference between methyl and alkyl radicals is then less easily accounted for; cf. A. F. Trotman-Dickenson, *Disc. Faraday Soc.*, **14**, 230 (1953).

alkyl radical undergoing chain transfer with chloroform or carbon tetrachloride, the poorer will be the electron donor properties of the alkyl radical and the smaller will be the polar effect facilitating the reaction.

TABLE IV

RELATIVE REACTIVITIES OF CARBON TETRACHLORIDE AND CHLOROFORM TOWARD VARIOUS RADICALS

Radical from	Ac ₂ O ₂ ^a	Ethy- lene ^b	Propy- lene	Vinyl ^c acetate	Styrene
Temp., °C.	100	70	100	60	60
C for CCl ₄		3.2	5-10	1.0	0.0092 ^d
C for CHCl ₃		3	1	0.016	0.00005 ^e
Ratio	0.09	1.0	5-10	60	180

^a F. G. Edwards and F. R. Mayo, *THIS JOURNAL*, **72**, 1265 (1950). ^b C's for both solvents are for long radicals. C for carbon tetrachloride is from ref. 13b, for chloroform from unpublished work of J. R. Little and G. S. Mills. The short chain values are also close together.^{18a} ^c J. T. Clarke, R. O. Howard and W. H. Stockmayer, private communication. ^d Ref. 3b. ^e R. A. Gregg and F. R. Mayo, *THIS JOURNAL*, **75**, 3130 (1953).

Consideration of the polar effect above suggests why most of the literature examples of solvent-monomer reactions to give 1:1 and 2:1 products involve hydrocarbons or ethers and polyhalides. Vinyl ethers and carbon tetrachloride give exceptionally high yields of 1:1 products.¹⁸ At the other extreme, with acceptor monomers and donor solvents, a few other illustrations of the polar effect can be found. Maleic anhydride reacts with alkylbenzenes¹⁹ in the presence of benzoyl peroxide at 100° to give substituted benzylsuccinic anhydrides, and 2-pentene reacts without catalyst at a higher temperature to give a substituted allylsuccinic anhydride.²⁰ Polychloroethylenes give small proportions of 1:1 adducts even with paraffins in the presence of peroxide,²¹ while tetrafluoroethylene reacts readily with cyclohexane to give 1:1, 2:1 and 3:1 products.²² Without assistance from the polar factor, high yields of very low molecular weight products in monomer-solvent reactions seem to be rare.

A third factor contributing to high yields of low molecular weight adducts is the size of the monomer. Steric hindrance is probably an important factor which limits the ability of isobutylene to polymerize by a free radical mechanism and of methallyl chloride to grow beyond a dimer.²³ With such monomers, reaction with solvent, to the extent that it occurs, can give only low molecular weight products,²⁴ but this reaction is a useful alternative to termination.

(18) S. A. Glickman, U. S. Patent 2,560,219 (1952); *C. A.*, **46**, 1023 (1952).

(19) W. G. Bickford, G. S. Fisher, F. G. Doller and C. E. Swift, *J. Am. Oil Chemists Soc.*, **25**, 251 (1948).

(20) K. Alder and H. Söll, *Ann.*, **565**, 57 (1949).

(21) L. M. Schmerling and J. P. West, *THIS JOURNAL*, **71**, 2015 (1949).

(22) P. L. Barrick, U. S. Patent 2,436,135 (1948); *C. A.*, **42**, 3771 (1948).

(23) K. E. Wilzbach, F. R. Mayo and R. Van Meter, *THIS JOURNAL*, **70**, 4089 (1948).

(24) W. E. Hanford and R. M. Joyce, U. S. Patent 2,440,800 (1948), state that a 3:1 mole ratio of isobutylene and carbon tetrachloride in an emulsion system at 100° (example XXI) gave a viscous oil whose chlorine content corresponded to 8.6 C₄H₈/CCl₄. Comparison with Table II suggests that either there is an error in their report or their product must have undergone hydrolysis or some other side reaction.

In general, to obtain good yields of low molecular weight products from a solvent and monomer, the alternating reactions, between monomer radical and solvent, and between solvent radical and monomer, must proceed readily in competition with both the polymerization and chain termination reactions. This condition requires that the transfer constant of the solvent be near or greater than unity, and is met most easily when one component is an electron donor in the transition state and the other an electron acceptor. With allylic monomers, reactive solvents and strong polar effects reduce termination by degradative chain transfer, and the situation is analogous to the acceleration of the polymerization of allyl acetate by maleic anhydride, the strong alternating effect greatly extending the kinetic chain length.²⁵ Monomers with conjugated substituents, with reactive double bonds and

(25) P. D. Bartlett and K. Nozaki, *THIS JOURNAL*, **68**, 1495 (1946).

unreactive radicals,^{11,26} will have smaller transfer constants for the same solvent than the unconjugated aliphatic monomers (*cf.* Table IV). Accordingly, only the most reactive solvents such as bromotrichloromethane⁷ or carbon tetrabromide,²⁷ with transfer constants near unity, give 1:1 products with styrene, while a wider range of solvents is effective with aliphatic monomers.¹³ The broken line in Fig. 1 plots results for styrene and carbon tetrachloride (transfer constant = 0.0115) at 76°. ^{3d} The low transfer constant prevents reaction of many solvent molecules per peroxide decomposed, although consumption of styrene is higher than for any other monomer shown.

(26) K. Nozaki, *Disc. Faraday Soc.*, **2**, 337 (1947).

(27) C. H. Bamford and M. J. S. Dewar, *ibid.*, **2**, 314 (1947); J. W. Breitenbach and H. Karlinger, *Monatsh.*, **82**, 245 (1951).

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LINGNAN UNIVERSITY]

Halogenation of Chelated Aryl Alkyl Ketones. I. Bromination of 2-Acetylnaphthol and Several of its Derivatives

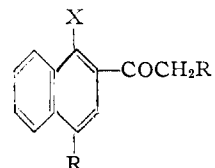
BY FREDERIC C. CHANG¹ AND YEN-SHANG YANG²

RECEIVED JULY 20, 1953

The finding that 4-nitro-2-acetylnaphthol is resistant to bromination led to a reinvestigation of the bromination of 2-acetylnaphthol. The results confirm literature reports that with excess bromine, the 4-bromo-2-acetylnaphthol formed is subsequently further brominated in the side chain, but if first isolated, it is found to resist bromination under identical previous conditions of solvent and temperature. This resistance to bromination is ascribed to chelation effects. Experimental evidence in support of this theory, and conditions under which the compound can be successfully brominated, are described.

During the course of unpublished early work on the naphthoquinone antimalarials,³ one of us (F.C.C.) found that 4-nitro-2-acetylnaphthol (II) unexpectedly resisted bromination even under somewhat forcing conditions,⁴ an observation which was not investigated further at the time. In resuming study of the problem, we were unable to reconcile the behavior of II with the seemingly straightforward α -bromination of 4-bromo-2-acetylnaphthol (III) (made from 2-acetylnaphthol (I)) as reported in the literature.^{5,6} For, although the nitro compound might be expected to undergo bromination less readily than the bromo derivative because of the greater electron attraction of the nitro group, as studies by Evans, Morgan and Watson⁷ of the bromination rates of various nuclear substituted acetophenones indicate, the extreme unreactivity of 4-nitro-2-acetylnaphthol in the reaction seemed implausible based merely on this

difference. An alternative explanation, that the nitro group exercises some unique effect, was even less attractive. We therefore decided to re-study the bromination and dibromination of 2-acetylnaphthol as a starting point in this investigation



Naphthols (X = OH)	Methyl ethers (X = OCH ₃)	Acetates (X = OCOCH ₃)	R	R'
I	VI	X	H	H
II			NO ₂	H
III	VII	XI	Br	H
IV	VIII	XII	Br	Br
V	IX	XIII	H	Br

(1) Department of Biochemistry, University of Tennessee, Memphis, Tenn.

(2) Based on the M.S. Thesis of Yen-shang Yang, Lingnan University, 1950.

(3) L. F. Fieser, M. T. Lefler and co-workers, *THIS JOURNAL*, **70**, 3151 (1948).

(4) In CCl₄ at room temperature, and under reflux; in acetic acid at room temperature, and under reflux. Alkaline bromination was not tried, as the α -mono-bromo compound was desired.

(5) K. Fries and R. Frelstedt, *Ber.*, **54**, 715 (1921).

(6) M. Akram, R. D. Desai and A. Kamal, *Proc. Indian Acad. Sci.*, **11A**, 139 (1940).

(7) D. P. Evans, V. G. Morgan and H. B. Watson, *J. Chem. Soc.*, 1167 (1935).

Our results indeed confirm the previous reports that I is readily brominated at room temperature to 4-bromo-2-acetylnaphthol (III), and by excess bromine to α ,4-dibromo-2-acetylnaphthol (IV). But we discovered that III does not react further with bromine under the identical previous conditions⁸ of temperature and solvent if the compound is first isolated. This apparent anomaly becomes clarified when the reactions involved in the dibromination of I are examined

(8) At reflux temperature in acetic acid, bromination does proceed (see experimental).