

3,3,3-trichloro-1-propylaminoacetate was heated at 105–110° in an open tube for 24 hours. The residue was crystallized from a large volume of ethanol, yielding a white powder, m.p. 266–267° dec. This product was insoluble in dil. hydrochloric acid and in refluxing 20% hydrochloric acid. The recovered solid from the latter decomposed at 270°. A small sample of the original product was sublimed at 0.2 mm. with some decomposition. The sublimed material decomposed at 271°.

Anal. Calcd. for $C_{10}H_{12}O_4N_2Cl_6$: C, 27.48; H, 2.75; N, 6.41. Found: C, 27.62; H, 2.69; N, 6.57.

An Attempt to Prepare 6-Trichloromethyl-2-morpholinone (VIIIa). 2-Acetoxy-3,3,3-trichloro-1-propylaminoacetic Acid (X).—The solid residue, obtained by refluxing 6.0 g. of ethyl 2-hydroxy-3,3,3-trichloro-1-propylaminoacetate with 150 ml. of 10% hydrochloric acid for three hours and evaporating to dryness under reduced pressure, was refluxed with 40 ml. of acetic acid and 10 ml. of acetyl chloride for 6 minutes. After adding 1 ml. more of acetyl chloride, the mixture was refluxed for 2 minutes longer. The residue from evaporating the reaction mixture under reduced pressure was crystallized from methanol-ether, giving a white, crystalline solid, m.p. 177–178° dec.

Anal. Calcd. for $C_7H_{11}O_4NCl_3$: C, 26.69; H, 3.49; N, 4.45. Found: C, 26.50; H, 3.63; N, 4.32.

The above solid was placed in water and sodium hydroxide was added with cooling in ice to pH about 7.5. The resulting solid was filtered and crystallized in succession from propanol-2, acetone and dry dioxane. The melting point of the material from each solvent was about the same, 111–119° with bubbling. If the melting point was retaken immediately it was about 116–122°. Droplets of liquid were noted on the upper part of the melting point tube. As this would indicate, this material was very hygroscopic. A heat and vacuum-dried sample gained weight rapidly in

an open tube on the micro-balance. The total gain in weight after 1.5 hours and the nitrogen analysis on this sample (3.92%) indicated about five molecules of water of hydration. Another analysis (reported below) was run on a sample dried in a weighing tube under vacuum over phosphorus pentoxide, stopping the weighing tube as quickly as possible after removing it from the drying apparatus. The material so dried was immediately soluble in dil. hydrochloric acid and in dil. sodium hydroxide and was precipitated from either solution by adjusting the pH to about 7.5.

Anal. Calcd. for 2-acetoxy-3,3,3-trichloro-1-propylaminoacetic acid dihydrate ($C_7H_{14}O_6NCl_3$): N, 4.44. Found: N, 4.43.

5-Trichloromethyloxazolidone (XI).—To a solution of 24 g. of 1,1,1-trichloro-3-aminopropanol-2 in 150 ml. of refluxing toluene was added 11.5 g. of ethylene carbonate. After refluxing for 15 hours and cooling, a viscous oil separated. The toluene was decanted from the oil and evaporated to 30 ml. Chilling and filtering afforded a solid which was crystallized from acetone-alcohol, giving 1.0 g. (3.7%) of white plates, m.p. 125–125.5°.

Anal. Calcd. for $C_4H_4O_2NCl_3$: C, 23.49; H, 1.96; N, 6.85. Found: C, 23.54; H, 2.20; N, 6.72.

N-Carbethoxy-1,1,1-trichloro-3-aminopropanol-2.—To a solution of 5.5 g. (0.031 mole) of 1,1,1-trichloro-3-aminopropanol-2 in 50 ml. of benzene was added an excess of ethyl chlorocarbonate. The mixture was refluxed for 50 hours, partially evaporated and chilled. Recrystallization of the resulting solid from benzene-acetone gave 6.03 g. (78.3%) of white plates, m.p. 72–73°.

Anal. Calcd. for $C_8H_{10}O_3NCl_3$: C, 28.78; H, 4.00; N, 5.59. Found: C, 28.71; H, 4.09; N, 5.49.

GREENCASTLE, IND.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

Solvent Effects and Initiator Efficiency in the Benzoyl Peroxide-Dimethylaniline System¹

BY CHEVES WALLING AND NORMAN INDICTOR

RECEIVED APRIL 17, 1958

The second-order reaction between benzoyl peroxide (Bz_2O_2) and dimethylaniline (DMA) has been followed in two ways: directly by measuring undecomposed peroxide, and indirectly, by observing *changing* polymerization rates while the pair was being used as polymerization initiator. The latter method was checked by using initiators of known decomposition rate and afforded a rapid reasonably precise method of obtaining initiator efficiency. Efficiencies were measured for bulk and solution polymerization from 0 to 80°. The reaction was strongly accelerated by pyridine; variation in rate with other solvents was also noted. The reaction of benzoyl peroxide with triethylamine yielded diethylvinylamine implying a new general path to enamine preparation. It is concluded that the tertiary amine-benzoyl peroxide reaction involves the initial formation of an unstable intermediate which may decompose by competing radical and non-radical forming processes.

Introduction

The second-order reaction between benzoyl peroxide and tertiary amines has been frequently studied,² mainly by Horner³ and co-workers and Imoto⁴ and co-workers. The products isolated^{3d}

(1) Taken from the dissertation of Norman Indictor submitted in partial fulfillment of the requirements of the Ph.D. degree, 1958. Support of this work by a research contract with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) For a more comprehensive review, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 590–594.

(3) (a) L. Horner and E. Schwenk, *Angew. Chem.*, **61**, 411 (1949); (b) L. Horner, *Ann.*, **566**, 69 (1950); (c) L. Horner and K. Sherf, *ibid.*, **573**, 35 (1951); **574**, 202 (1951); (d) L. Horner and C. Betzel, *ibid.*, **579**, 175 (1953); (e) L. Horner and H. Junkermann, *ibid.*, **591**, 53 (1955); (f) L. Horner, *J. Polymer Sci.*, **18**, 438 (1955).

(4) (a) M. Imoto and S. Choe, *J. Polymer Sci.*, **15**, 485 (1955); (b) M. Imoto, T. Otsu and K. Kimura, *ibid.*, **15**, 475 (1955); (c) M. Imoto, T. Otsu and T. Ota, *Makromol. Chem.*, **16**, 10 (1955); (d) M. Imoto, S. Choe and H. Taketsugi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **58**, 451 (1955); (e) M. Imoto and K. Takemoto, *J. Polymer Sci.*, **19**, 579 (1956).

from dimethylaniline (after aqueous treatment) are mainly benzoic acid, methylaniline and formaldehyde plus smaller amounts of *p*-benzoyloxy-dimethylaniline and *p,p'*-di-(dimethylamino)-diphenylmethane. Rate studies of the reaction have indicated that electron donor groups on the amine accelerate the reaction,^{3c} as do electron acceptor groups on the peroxide.^{2a,e}

The system Bz_2O_2 -*t*-amine has been found to initiate polymerization^{3b,4,6} with a variety of monomers. The observed relationship

$$R_p \propto [Bz_2O_2]^{1/2} \text{ to } (\text{amine})^{1/2}$$

is consistent with a bimolecular radical forming process. Meltzer and Tobolsky⁵ have noted that with styrene the relation between polymerization

(5) T. Meltzer and A. Tobolsky, *THIS JOURNAL*, **76**, 5178 (1954).

(6) K. Noma, O. Nisiura and A. Ichiba, *Chem. High Polymer Japan*, **10**, 231 (1953); J. Lal and R. Green, *J. Polymer Sci.*, **17**, 403 (1955).

rate and polymer molecular weight is that calculated for chain termination by the usual interaction of growing polymer chains. Little^{3b} or no^{4b} nitrogen is found in the polymers.

We have investigated the reaction from the point of view of solvent effects and the quantitative effectiveness of the pair as a polymerization initiator.

Results

Effect of Solvents on the DMA-Bz₂O₂ Reaction.—Rates of decomposition of Bz₂O₂ in the presence of excess DMA in various solvents at 0° were determined iodometrically as described in the Experimental section. Under these conditions the decomposition is pseudo first order and rate constants have been calculated from the expression

$$-d[\text{Bz}_2\text{O}_2]/dt = k_2[\text{Bz}_2\text{O}_2][\text{DMA}]_0 \quad (1)$$

Results are summarized in Tables I and II. All units are in moles, liters and seconds.

TABLE I

EFFECT OF SOLVENTS ON THE DMA-Bz₂O₂ REACTION AT 0°

| Solvent | All runs in air except as indicated | | |
|----------------------------|-------------------------------------|--|----------------------------------|
| | (DMA) ₀ | (Bz ₂ O ₂) ₀ | k ₂ × 10 ⁴ |
| Pyridine | 0.5 | 0.095 | 120 ± 30 |
| Chloroform ^a | .2 | .1 | 19 ± 5 |
| Chloroform | .5-1.0 | .022-0.1 | 5.2 ± 0.6 |
| Benzene ^b | 1.0 | .086 | 15.4 |
| Ethanol | 0.396-0.79 | .024 | 9.4 |
| Ethyl acetate ^b | 1.0-2.0 | .090 | 6.0 ± .3 |
| Ethyl acetate | 0.5 | .098-.102 | 1.8 ± .1 |
| Styrene ^a | .5-1.0 | .079-.090 | 2.8 ± .1 |
| Styrene | 1.0 | .09 | 2.8 ± .1 |
| Styrene ^b | 0.112-0.391 | .031 | 2.8 ± .15 |
| Acetone | .5-2.0 | .09 | 2.1 ± .2 |

^a Under nitrogen. ^b *In vacuo*.

TABLE II

EXPERIMENTS IN MIXED SOLVENTS AT 0°
All experiments in air with equal parts by volume of solvents,
0.5 M DMA unless indicated

| Solvents | (Bz ₂ O ₂) ₀ | k ₂ × 10 ⁴ |
|--|--|----------------------------------|
| Acetone-water | 0.094 | 6.1 |
| Chloroform-pyridine 1:3 | .106 | 7.7 |
| Chloroform-acetic acid | .091 | 3.23 |
| Chloroform-benzoic acid (0.2 M) | .103 | 5.77 |
| Benzene-styrene | .098 | 3.88 |
| Ethyl acetate-styrene | .097 | 3.98 |
| Acetone-styrene | .094 | 4.36 |
| Pyridine-styrene | .095 | 9.19 ^a |
| Nitrobenzene-styrene | .1-0.108 | 6.2 ± 0.2 ^b |
| Chloroform-styrene (1 M) | .080 | 13.6 |
| Chloroform-styrene (5 M) | .081 | 5.8 |
| Chloroform-diethyl maleate (2 M) | .059 | 12.1 |
| Chloroform-methyl methacrylate (1.9 M) | .099 | 5.9 |
| Chloroform-acrylonitrile (1 M) | .092 | 11.5 |

^a [DMA]₀ = 0.3135. ^b [DMA]₀ = 0.5-1.0.

Polymerization Experiments.—Russell⁷ has described an ingenious technique by which the rate of decomposition of an initiator can be determined

(7) G. Russell, *THIS JOURNAL*, **78**, 1044 (1956).

by following the changing rate of a resulting radical chain process (in his case, hydrocarbon oxidation) through several initiator half-lives. Application of the same approach to polymerizations initiated by the Bz₂O₂-DMA system has enabled us to extend measurements of the rate of the Bz₂O₂-DMA reaction to very low concentrations and higher temperatures and simultaneously determine the efficiency of the system as a polymerization initiator.

If it is assumed that the polymerization of styrene or methyl methacrylate follows the usual rate law

$$-d[M]/dt = R_p = k_p[M](R_i/2k_t)^{1/2} \quad (2)$$

where the symbols have their usual significance, and

$$R_i = 2ek_2[\text{Bz}_2\text{O}_2][\text{DMA}]_0 \quad (3)$$

where *e* represents the efficiency of the system in starting chains, we obtain for the variation in polymerization rate with time

$$\log R_p = \log R_{p0} - k_2[\text{DMA}]_0/2(2.303) \quad (4)$$

In applying equation 4, polymerization rates were followed dilatometrically in the absence of air. Figure 1 illustrates the results of a typical run,

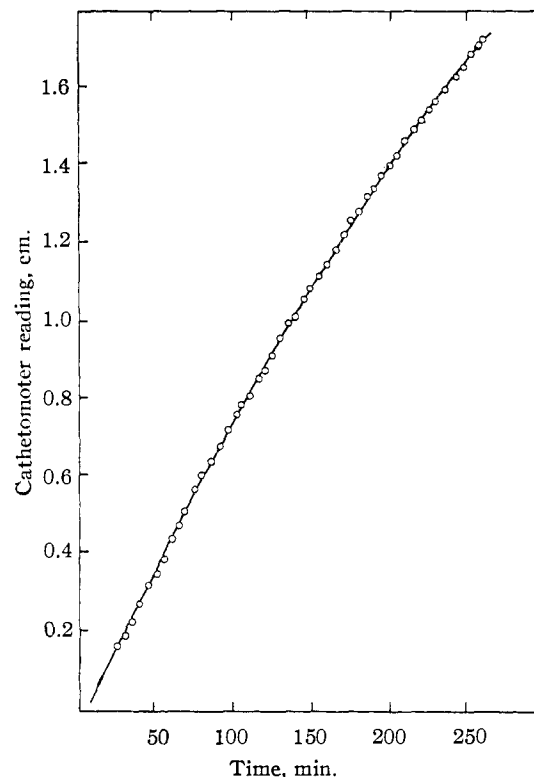


Fig. 1.—Polymerization of styrene initiated by Bz₂O₂-DMA at 0° (first run, Table III).

and *k*₂'s were calculated by least squares analysis of the data. In cases where Bz₂O₂ was present in excess, [DMA]₀ was replaced by [Bz₂O₂] in (4). Once *k*₂ is known, *e* may be obtained from the relation

$$e = R_{p0}^2 k_t / k_p k_2 [M]^2 [\text{Bz}_2\text{O}_2]_0 [\text{DMA}]_0 \quad (5)$$

The only additional quantity needed is the ratio *k*_t/*k*_p², and values were taken from the data of

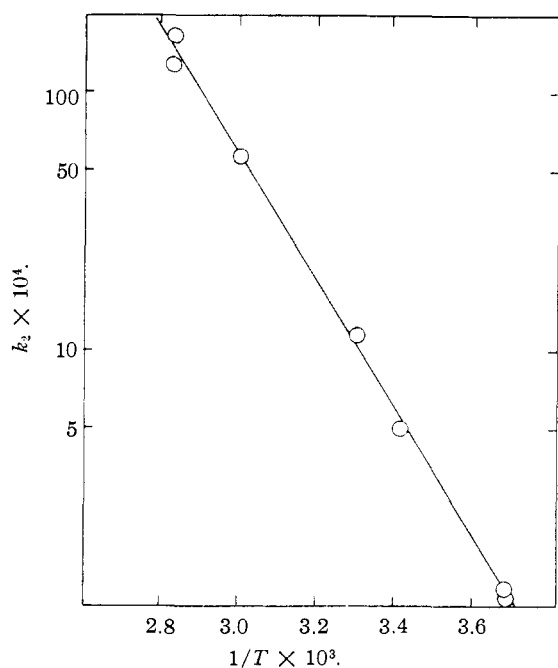


Fig. 2.—Temperature dependence of Bz_2O_2 -DMA reaction in styrene; data of Table III.

Tobolsky, *et al.*,⁸ assuming chain coupling for styrene and disproportionation for methyl methacrylate.⁹ Values for k_2 and ϵ are listed in Tables III and IV. A plot of $\log k_2$ vs. $1/T$, Fig. 2, gives the thermodynamic quantities $\Delta H^\ddagger = 11.0$ kcal./mole, $\Delta S^\ddagger = -9.9$ e.u.

TABLE III
POLYMERIZATIONS OF STYRENE (OR METHYL METHACRYLATE^a)

| Temp. | $(Bz_2O_2)_0$ | $(DMA)_0$ | $R_{p0} \times 10^3$ | $k_2 \times 10^4$ | ϵ |
|-----------------|----------------------|-----------|----------------------|-------------------|------------|
| 0 | .001 | 0.50 | 0.38 | 1.2 | 0.22 |
| 0 | .002 | 1.00 | 0.89 | 1.1 | .21 |
| 0 | .025 | 1.000 | 3.21 | 1.6 | .15 |
| 0 | .050 | 1.000 | 4.29 | 2.4 | .14 |
| 0 | .100 | 1.000 | 10.7 | 3.1 | .21 |
| 0 | .100 | 1.000 | 10.7 | 2.8 | .24 |
| 0 | .250 | 0.00625 | 0.87 | 1.3 | .23 |
| 0 | .250 | .0313 | 2.0 | 2.3 | .13 |
| 20 | .005 | .500 | 4.7 | 5.0 | .22 |
| 30 | .002 | .500 | 7.7 | 11.7 | .24 |
| 40 ^a | .00049 | .440 | 36.0 | 57 | .16 |
| 60 ^a | .00049 | .0922 | 33.5 | 110 | .09 |
| 60 | .00047 | .0049 | 1.31 | 57 | .12 |
| 80 | .00046 | .00921 | ... | 170 | ... |
| 80 | .000046 | .0921 | 4.12 | 130 | .10 |
| 80 | .0046 | | ... | 0.42 ^c | ... |
| 80 | .0046 | | 15.7 | 0.31 ^c | .58 |
| 80 | .000184 ^b | | 8.0 | 1.76 ^c | .62 |

^a Methyl methacrylate. ^b Azobisisobutyronitrile rather than Bz_2O_2 as initiator. ^c First-order rate constants for thermal decomposition in absence of DMA.

The foregoing treatment requires that ϵ is constant for a given run. This assumption appears

(8) A. V. Tobolsky and J. Offenbach, *J. Polymer Sci.*, **16**, 311 (1955); A. V. Tobolsky and T. E. Ferrington, *J. Colloid Sci.*, **10**, 536 (1955).

(9) J. C. Bevington, H. W. Melville and R. P. Taylor, *J. Polymer Sci.*, **12**, 449 (1954).

TABLE IV

STYRENE POLYMERIZATIONS IN SOLVENTS AT 0°
4.44 M styrene, 1.00 M DMA in all runs

| Solvent | $(Bz_2O_2)_0$ | $R_{p0} \times 10^3$ | $k_2 \times 10^4$ | ϵ |
|---------------|---------------|----------------------|-------------------|------------|
| Benzene | 0.005 | 0.38 | 0.9 | 0.07 |
| Benzene | .010 | .59 | 1.0 | .08 |
| Benzene | .005 | .38 | 1.0 | .07 |
| Ethyl acetate | .005 | .40 | 1.1 | .07 |
| Pyridine | .002 | .61 | 1.5 | .29 |
| Pyridine | .003 | .72 | 1.4 | .29 |
| Acetone | .005 | .62 | 1.6 | .11 |
| Chloroform | .005 | .42 | 1.8 | .05 |
| Nitrobenzene | .005 | No polymerization | | |

valid since there is no notable trend in ϵ with changes by DMA and Bz_2O_2 concentration, and also since the results of any one give a good fit to equation 4. It also should be noted that, in all experiments, extent of polymerization was small enough so that monomer concentration remained constant, and it is assumed in (3) that each reaction of DMA and Bz_2O_2 leads to the production of two radicals (see below). A further check of the validity of the whole method appears in the last three experiments of Table III. Here polymerization was initiated by Bz_2O_2 and azobisisobutyronitrile in the absence of DMA, and the calculated decomposition rates and ϵ 's are in good agreement with literature values.¹⁰

Discussion

Solvent Effects.—The results of Tables I and II show that the rate of DMA- Bz_2O_2 reaction changes significantly with solvent. As much as 60-fold change has been observed in going from acetone to pyridine. Most solvents used give results within the tenfold range of $2-20 \times 10^{-4}$ liter/mole sec. and only pyridine accelerates the rate beyond that range. Acetic acid depresses the rate in chloroform, but only to about the level observed in the presence of other carbonyl compounds such as acetone and ethyl acetate, and small amounts of benzoic acid have no significant effect.

Tables I and II include data on reaction rates in the presence of vinyl monomers. In chloroform the rate is depressed by styrene, but increased by diethyl maleate and, to a lesser degree, by methyl methacrylate.

Effect of Oxygen.—Horner has made two observations concerning the effect of oxygen^{3e} on the measured reaction rate: first, the second-order rate constant for peroxide disappearance is greater in a nitrogen atmosphere than in an oxygen atmosphere and, second, the appearance of benzoic acid is faster in an oxygen atmosphere than the disappearance of peroxide measured iodometrically. Horner's conclusion is that oxygen permits the formation of titratable peroxide, but Horner's efforts to isolate such a compound have been unsuccessful.

Table I shows cases in which the exclusion of oxygen from the system has raised the measured decomposition rate; but the presence of styrene eliminates this effect. This implies that, if Horner's conclusions are correct, the titratable peroxide never has the opportunity of forming in

(10) Cf. ref. 2, pp. 478 and 512.

the presence of styrene. The polymerizing styrene traps the oxygen, producing non-titratable peroxides in a manner described in the work of Miller and Mayo.¹¹

Polymerizations. The measurements of Tables III and IV extend reaction rates to very low peroxide concentrations, and also give data on the efficiency of the DMA-Bz₂O₂ reaction in initiating polymerization. The data of Table III indicate a small but significant rise in the bimolecular rate constant, *k*₂, with increasing concentration. Runs at comparable concentrations show good agreement with the iodometrically determined *k*₂'s in Table I.

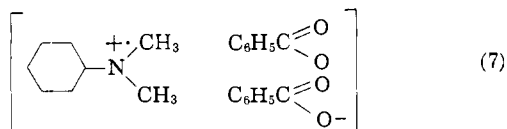
The only literature values to which the efficiencies here presented can be compared are in a paper by Imoto^{4c} which appeared while this work was in progress. Imoto's data for bulk styrene polymerizations at 50° gave efficiencies of 0.25 ± 0.05. Initial rates of polymerization were obtained by gravimetric isolation of polystyrene and the initiator disappearance rates were obtained iodometrically. Our data present efficiencies over a temperature range between 0 and 80° and indicate a slight decline (from about 0.25 at 0° to about 0.10 to 80°) with rising temperature.

The values of *k*₂ obtained from runs using methyl methacrylate were approximately double those observed in styrene, paralleling the results of Table II, but efficiencies of chain starting appear comparable.

In the presence of solvents (except pyridine) there is a pronounced decrease in the calculated efficiency of chain starting. Similar decreases have been noted in other styrene polymerizations (usually at higher dilutions) but their cause remains rather obscure.¹²

Finally, the very high rates of the DMA-Bz₂O₂ reaction at room temperature and above clearly show the reason for the frequently noted observation that this initiator system tends to produce a rapid initial polymerization which stops short of completion. Plainly at these temperatures the initiator is exhausted rapidly.

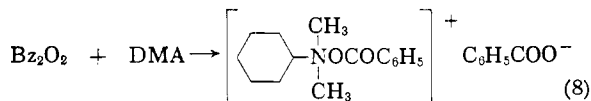
Mechanism of the Bz₂O₂-DMA Reaction.—Although it seems clear that Bz₂O₂ and DMA undergo a bimolecular reaction giving rise to free radicals, the exact nature of the process is certainly controversial. Thus Horner^{3f} has proposed as the rate-determining step the formation of a "complex"



which subsequently gives rise to the observed products, while Imoto^{4a} has suggested the reversible formation of a complex which subsequently decomposes into free radicals.

It seems plausible to us that the rate-controlling step is a nucleophilic displacement on the peroxide by DMA to yield a quaternary hydroxylamine derivative

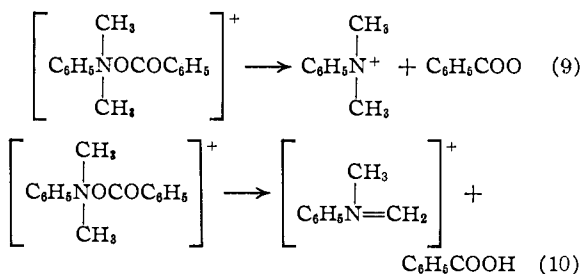
(11) A. A. Miller and F. R. Mayo, *THIS JOURNAL*, **78**, 1017 (1956).
 (12) See ref. 2, pp. 72-73.



Such a formulation parallels that proposed for the bimolecular reaction of peroxides and phenols¹³ and, as it leads to an ionic product, should have a considerable negative entropy of activation. As previously has been pointed out,² it also accounts for the accelerating effects of electron-supplying groups on the amine and electron-withdrawing groups on the peroxide, and parallels a plausible formulation of three other reactions: the reaction of peroxides with secondary amines, the formation of amine oxides in the presence of hydrogen peroxide, and the initiation of polymerization by amine oxides in the presence of acylating agents.¹⁴

On the other hand, it must be admitted that, while a polar process such as (8) should show a solvent-dependent rate, there is little correlation in the results we report here with any such solvent properties as dielectric constant or solvating ability or with the mechanistically parallel Menschutkin reaction.¹⁵ Conceivably this is a case where entropy and heat effects work contrary to each other in changing media, but a similar difficulty confronts any of the other formulations mentioned. Incidentally, kinetics provide no means of detecting the existence of a fast equilibrium with some sort of complex prior to (8) as Imoto suggests.^{4a} In such a case our *k*₂ would represent a composite quantity each term of which might be somehow solvent dependent. Similar rather inscrutable solvent effects have been noted in Hammond's¹⁶ studies of autoxidation inhibition, here believed to involve amine-peroxy radical complexes.

The product of reaction (8) has only transient existence and decomposes by at least two possible paths



Reaction (9) which gives Horner's intermediate represents a free radical path and would account for the initiation of polymerization. Since no significant amount of nitrogen is found in the resulting polymers the amine fragment may well disappear by reaction with further peroxide.

(13) C. Walling and R. B. Hodgson, Jr., *THIS JOURNAL*, **80**, 228 (1957).

(14) V. Boekelheide and D. L. Harrington, *Chemistry & Industry*, 1423 (1955).

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 347; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 214.

(16) G. S. Hammond, C. E. Boozer and C. E. Hamilton, *THIS JOURNAL*, **77**, 3238 (1955).

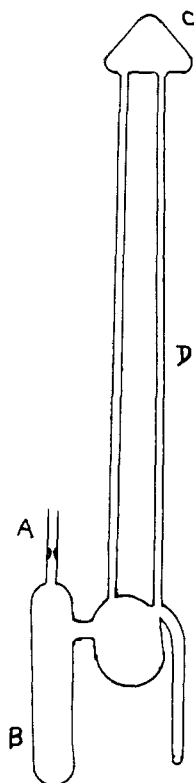
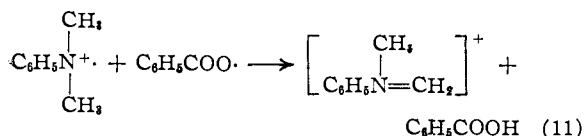
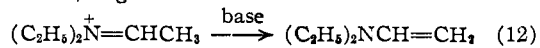


Fig. 3.—Dilatometer for polymerization studies.

Reaction 10 represents a non-radical breakdown, and would account for the low efficiency of the system as a polymerization initiator. Admittedly, the same products could arise from a radical disproportionation



more nearly as suggested by Horner but, in the latter case, the reaction would have to occur in the same solvent "cage" as reaction 9, since otherwise (11) would compete with the initiation of polymerization and the efficiency of the latter would not show the independence of Bz_2O_2 and DMA concentration actually observed. In either case, hydrolysis of the quaternary imine leads to the major products isolated: dealkylated amine and formaldehyde. Interestingly, in the case of longer chain amines, the quaternary imine is actually the conjugate acid of the corresponding enamine, which should be produced on treatment with base, *e. g.*



We find that when triethylamine is treated with

benzoyl peroxide and the reaction mixture treated with piperidine and distilled, a colorless fraction, b.p. 65–71°, is obtained with an infrared peak at 6.1 μ characteristic of the enamine structure,¹⁷ and which polymerizes on standing essentially as described in the literature.¹⁸

Experimental

Materials.—Benzoyl peroxide was recrystallized from chloroform-methanol. Monomers were freed of inhibitor by distillation at water-pump pressure. Solvents were redistilled commercial material. Dimethylaniline was purified according to the procedure of Tobolsky and Meltzer.⁵

Iodometric rates were carried out in a 0° thermostat fashioned from a Dewar flask filled with ice washed in distilled water and stirred by pumping precooled air through it. Control was $\pm 0.01^\circ$. Analysis of aliquots was by titration using potassium iodide in acetic acid and standard thiosulfate.

Polymerizations of styrene and methyl methacrylate were carried out in an all-Pyrex dilatometer (Fig. 3) designed for convenient degassing. An aliquot of a solution of Bz_2O_2 in chloroform was pipetted through A into reservoir B. The chloroform was evaporated carefully under reduced pressure and 50 ml. of monomer solution containing amine was transferred into B with a syringe. Reservoir B was submerged in a Dry Ice-trichloroethylene mixture. The system was degassed three or four times with thawing *via* the opening A by a mercury diffusion pump and sealed at the constriction near A at a pressure of 1–2 μ . The liquid in reservoir B is then thawed and shaken to ensure complete solution of the initiator. The entire dilatometer is then inverted and held at an angle such that the liquid in reservoir B pours through one of the capillary tubes (D, the one closer to the reservoir) filling bulb C. The capillary tubes D are made of 0.05 mm. Trubore glass tubing 20 cm. long and are about 1% of the volume of C. When the bulb C and the capillary tubes D are filled (capacity about 40 ml.) the excess solution is retained in B. Bulb C is thermostated at the desired temperature and the liquid in bulb C expands or contracts according to the thermostat temperature. Liquid can be removed from bulb C or added from the reservoir by tilting the dilatometer until a convenient level is reached somewhere along the capillary. In this position (inverted Fig. 3) the dilatometer is placed firmly in a thermostat and contractions recorded at time intervals. The contractions are measured by means of a cathetometer whose vernier is calibrated to read changes of 0.005 cm. Equilibration of liquid in reservoir B is taken as zero time. Since obviously no measurements can be made during transfer to bulb C, polymerization rates cannot be measured at zero time but must be extrapolated.

Isolation and Identification of Diethylvinylamine.—Five grams of triethylamine in 150 cc. of pyridine was added to 12 g. of Bz_2O_2 maintaining 25–30° in the reaction flask by surrounding it with ice. The dark mixture was permitted to stand overnight stoppered.

A few ml. of the reaction mixture failed to liberate iodine from a glacial acetic acid-KI solution indicating that Bz_2O_2 had decomposed completely.

About 15 ml. of piperidine was added to the reaction mixture and the entire mixture was distilled through an insulated Vigreux column at atmospheric pressure. The first fraction, collected clear and colorless, came over at 65–71°, had a very acrid odor, and gave a peak in the infrared at 6.1 μ . Upon standing overnight the distillate became gelatinous and yellow-brown.

NEW YORK 27, N. Y.

(17) N. J. Leonard and V. W. Cash, *THIS JOURNAL*, **76**, 2781 (1954).

(18) K. H. Meyer and H. Hopff, *Ber.*, **54B**, 2106, 2274 (1921); C. Mannich and H. Davidson, *ibid.*, **69B**, 2106 (1936).