868. *Reactions of Peroxides in* NN-*Dimethylformamide Solution. Part II.*[1] *The Decomposition of Benzoyl Peroxide in the Presence of Chloride Ions.*

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Benzoyl peroxide reacts rapidly with ionic chlorides in *NN*-dimethylformamide or dichloroethane solution. The primary reaction is considered to be the nucleophilic displacement (1) forming benzoyl hypochlorite and benzoate. The hypochlorite may react further with chloride to give molecular chlorine and benzoate or may decompose homolytically into benzoyloxy-radicals and chlorine atoms. The former reaction is reversible, since it has been shown that chlorine reacts with lithium benzoate to give benzoyl hypochlorite as a yellow oil. Secondary reactions involving the solvents and the primary products are discussed. The implications of this work with respect to the mechanism of the Hunsdiecker reaction are considered briefly. Although free radicals are produced in some circumstances, mixtures of benzoyl peroxide and chlorides are not initiators of vinyl polymerization.

DURING an investigation of vinyl polymerization in *NN*-dimethylformamide solution in the presence of salts a rapid reaction between benzoyl peroxide and ionic chlorides was noticed. For example, in the presence of 0·2m-lithium chloride at 60° the half-life of benzoyl peroxide is less than one minute, compared with 154 minutes in the absence of salt.[1] A reaction under these conditions is, of course, not unexpected since treatment with iodides in acetone solution is the basis of the estimation of peroxides. It seemed possible that the chloride–peroxide reaction might have analogies with the rapid decomposition of benzoyl peroxide sensitized by some tertiary amines [2] and might be an effective source of free radicals for initiating vinyl polymerization.

Edwards [3] and Symons [4] recently proposed that reactions between halide ions and hydrogen peroxide in aqueous solution are nucleophilic displacements producing the intermediate hydrogen hypohalite. The primary reaction between benzoyl peroxide and ionic chlorides appears to be similar; under suitable conditions the hypohalite may decompose into free radicals, but there is no evidence that these are produced in the primary reaction.

RESULTS AND DISCUSSION

Investigation of the decomposition of benzoyl peroxide by ionic chlorides is restricted by the lack of suitable non-reactive solvents. Interaction of the solvent with the primary products makes their identification and analysis difficult. Nevertheless, preliminary observations of the reaction in *NN*-dimethylformamide and dichloroethane indicated that the primary process is the nucleophilic displacement:

$$(\mathrm{Ph{\cdot}CO{\cdot}O})_2 + \mathrm{Cl}^- \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OCl} + \mathrm{Ph{\cdot}CO{\cdot}O}^- \quad . \; . \; . \; . \; . \; . \; . \; (1)$$

Later discussion will show that a reaction scheme consistent with all the experimental observations may be constructed on the basis of this reaction.

General Features of the Reaction in NN-*Dimethylformamide.*—The course of the decomposition of benzoyl peroxide in *NN*-dimethylformamide solution at 60° with different concentrations of lithium chloride is shown in Fig. 1. Initial rates of decomposition are proportional both to the peroxide and chloride concentrations but the proportionality does not hold in the later stages of the reaction. Similar results were obtained at 25°, giving an

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[1] Part I, Bamford and White, *J.*, 1959, 1860.

[2] Horner and Schwenk, *Angew. Chem.*, 1949, **61**, 411.

[3] Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 1540.

[4] Symons, *J.*, 1955, 273.

apparent activation energy for the early part of the reaction of 19·4 kcal. mole^{-1} compared with 28·3 kcal. mole^{-1} for the thermal decomposition of benzoyl peroxide in the absence of chloride.[1]

A characteristic feature of the reaction is the appearance of a yellow colour due to liberation of molecular chlorine followed by its complex-formation with chloride to give Cl_3^- ions. This complex does not react readily with benzoyl peroxide. In Fig. 2, peroxide, chloride, and chlorine concentrations are shown as a function of time. The chlorine concentration reaches a maximum when most of the peroxide has decomposed and then decreases slowly. The yield of chlorine per mole of peroxide decomposed is greater than would be expected if chlorine were formed solely from the homolysis of benzoyl hypochlorite resulting from reaction (1), followed by recombination of chlorine atoms as in (2):

$$\left.\begin{array}{ll} Ph\cdot CO\cdot OCl \longrightarrow Ph\cdot CO\cdot O\cdot + Cl\cdot & (a) \\ 2Cl\cdot \longrightarrow Cl_2 & (b) \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

FIG. 1. *Decomposition of benzoyl peroxide in* NN-*dimethylformamide at* 60° *in the presence of lithium chloride at concentrations shown. Initial peroxide concentration* 0·017 *mole l.*$^{-1}$.

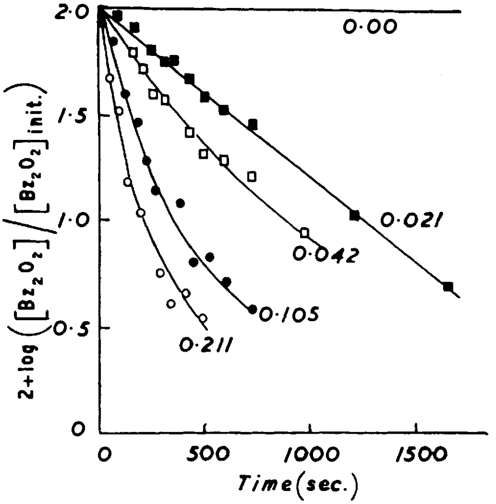
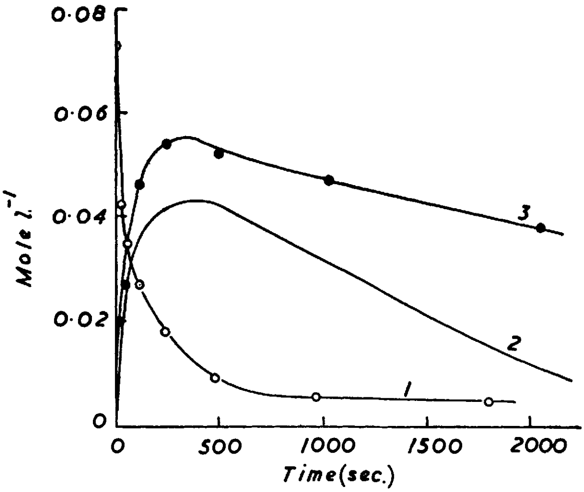


FIG. 2. *Peroxide, chlorine, and chloride concentrations as a function of time in the decomposition of benzoyl peroxide in* NN-*dimethylformamide at* 60° *in the presence of lithium chloride. Concentration* (*mole l.*$^{-1}$) *of* (1) *peroxide,* (2) *chlorine*; (3) *chloride consumed* (*mole l.*$^{-1}$).



Such a mechanism predicts a yield of 0·5 mole of chlorine per mole of peroxide decomposed, whereas the observed yields after 20% and 40% reaction are 1·0 and 0·75 respectively in the experiments of Fig. 2. The high yield can be explained if reaction (3*a*) between benzoyl hypochlorite and chloride occurs:

$$Ph\cdot CO\cdot OCl + Cl^- \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Ph\cdot CO\cdot O^- + Cl_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

A reaction of this type has already been postulated in another connexion by Anbar and Ginsburg,[5] Edwards,[3] and Symons.[4]

The increase in chloride concentration after 300 sec. (Fig. 2) arises either from a reaction between chlorine and *NN*-dimethylformamide (forming hydrogen chloride) or from reaction (3*b*) above. The reversibility of reaction (3) is considered below.

Lithium benzoate is formed in the primary reaction (1), and removed by reaction (3*b*). Benzoic acid, which also appears among the products, may arise in two ways: (i) from lithium benzoate by reaction with hydrogen chloride, (ii) by attack of benzoyloxy-radicals

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[5] Anbar and Ginsburg, *Chem. Rev.*, 1954, **54**, 925.

on the solvent. A further product, *N*-benzoyloxymethyl-*N*-methylformamide (I), has been isolated. This is a major product of the thermal decomposition of benzoyl peroxide in *NN*-dimethylformamide [1] and arises from the reactions shown in (4):

$$\left.\begin{array}{rl} \mathrm{Ph{\cdot}CO{\cdot}O{\cdot} + H{\cdot}CO{\cdot}NMe_2} & \longrightarrow \mathrm{Ph{\cdot}CO_2H + H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}}\ (a) \\ \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot} + (Ph{\cdot}CO{\cdot}O)_2} & \longrightarrow \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}O{\cdot}COPh\ (I) + Ph{\cdot}CO{\cdot}O{\cdot}}\ (b) \\ \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot} + Ph{\cdot}CO{\cdot}O{\cdot}} & \longrightarrow \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}O{\cdot}COPh}\ (c) \end{array}\right\} \quad . \quad . \quad (4)$$

A similar mechanism could account for the formation of the amide (I) in the present system, the initial benzoyloxy-radicals being formed from the homolysis of benzoyl hypochlorite (2*a*).

Since hydrogen chloride may be produced by side reactions the ratio of benzoic acid to lithium benzoate in the products is not particularly helpful in elucidating the reaction mechanism. By adding styrene to act as a chlorine scavenger it was hoped to eliminate some of the complications arising from secondary reactions of chlorine. Table 1 gives the combined yield of benzoic acid and lithium benzoate for different initial concentrations of reactants.

TABLE 1.

$[Cl^-]$ initial (mole $l.^{-1}$)	[Peroxide] initial (mole $l.^{-1}$)	[Styrene] initial (mole $l.^{-1}$)	Molar yield of $Ph{\cdot}CO_2H$ + $Ph{\cdot}CO_2Li$ as % of peroxide decomposed
0·51	0·20	0	137
Very low	0·20	2·5	157
0·13	0·18	0·79	166
0·95	0·19	0·79	172
1·25	0·22	0·79	184
0·36	0·14	2·5	187
0·86	0·13	2·5	190

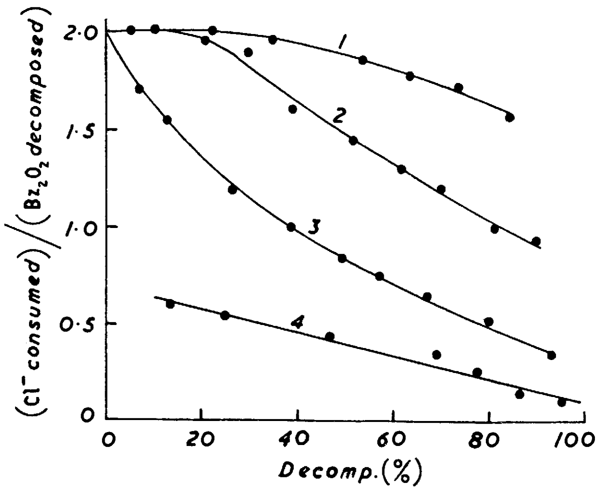
If the reaction proceeded entirely according to (1) and (3*a*) the molar yield of lithium benzoate would be 200%. Table 1 shows that in the absence of styrene the combined yield of lithium benzoate and benzoic acid is well below this. The yield is higher in the presence of styrene; further, the figures suggest that it increases with increasing Cl^- concentration at constant styrene concentration. These observations are consistent with the existence of the equilibrium (3). In the absence of styrene the equilibrium is established; any benzoyl hypochlorite which does not ultimately give benzoate by (3*a*) must decompose according to (2*a*). The resulting benzoyloxy-radicals enter into reaction (4) with the formation of the amide (I) which accounts for the low combined yield of benzoic acid and lithium benzoate in the absence of styrene. It should be noted that *NN*-dimethylformamide radicals may arise not only from reaction (4*a*), but also from the analogous reaction (5):

$$\mathrm{Cl{\cdot} + H{\cdot}CO{\cdot}NMe_2 \longrightarrow HCl + H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the presence of a sufficient concentration of styrene, reaction (3*b*) is effectively eliminated and the hypochlorite decomposes mainly according to (3*a*). Clearly, the homolysis (2*a*) is reduced in importance in the presence of styrene, with a corresponding decrease in the yield of amide (I) and an increase in the combined yield of benzoic acid and benzoate. The observation that the combined yield is somewhat lower than 200% under these conditions is understandable if a little of the hypochlorite adds directly to styrene. In this situation the yield should increase with increasing $[Cl^-]$, as appears to be so from Table 1. If this explanation is to be satisfactory the reaction of the hypochlorite with chloride must be much faster than that with styrene at a similar concentration.

These ideas are further supported by experiments in which the concentration of chloride used per mole of peroxide decomposed was measured as a function of time (Fig. 3). In the absence of styrene, when the equilibrium (3) has been established, benzoyl hypochlorite will be lost only by reaction (2*a*); hence less than one equivalent of Cl^- should be used per mole of peroxide decomposed [since some Cl^- will be regenerated, *e.g.*, by reaction (5)]. This is so in practice in the later stages of the reaction. Initially, however, reaction (3*a*) is faster than (3*b*) and the chloride consumption should approximate to two equivalents per mole of peroxide, as is observed. In the presence of styrene, the consumption of Cl^- is also relatively high throughout the whole reaction on account of the suppression of reaction (3*b*). In curve 1 of Fig. 3, referring to a high initial $[Cl^-]$, the consumption of Cl^- is almost constant at 2 moles per mole of peroxide up to 55% decomposition of peroxide. At a lower $[Cl^-]$ (curve 2) the consumption falls off more rapidly from 2 to approximately 1 mole per mole owing to the depletion of chloride as the reaction proceeds. At very low $[Cl^-]$, direct addition of benzoyl hypochlorite to styrene (resulting in a Cl^- consumption of 1 mole per mole) is able to compete with reaction (3*a*). The addition of lithium benzoate (in the absence of styrene) results in relatively rapid attainment of equilibrium (3) and, as would be expected, reduces the consumption of chloride (curves 3 and 4, Fig. 3).

FIG. 3. *Chloride consumed per mole of benzoyl peroxide decomposed as a function of the percentage decomposition of peroxide for the reaction in* NN-*dimethylformamide at* 60° *in the presence of lithium chloride.*



Initial concentrations: (1) $[Cl^-] = 0{\cdot}104$, $[Bz_2O_2] = 0{\cdot}017$, [styrene] = 0·4 mole $l.^{-1}$. (2) $[Cl^-] = 0{\cdot}033$, $[Bz_2O_2] = 0{\cdot}018$, [styrene] = 0·4 mole $l.^{-1}$. (3) $[Cl^-] = 0{\cdot}032$, $[Bz_2O_2] = 0{\cdot}020$. (4) As in (3), but with [lithium benzoate] = 0·48 mole $l.^{-1}$.

The Reaction between Chlorine and Lithium Benzoate.—Reaction (3*b*) is analogous to the first stage of the Hunsdiecker reaction between the silver salt of a carboxylic acid and a halogen. It is generally considered that the primary products in the Hunsdiecker reaction are the corresponding acyl hypohalite and silver halide; the evidence for this is clear [5] but there does not seem to be any record of the isolation of benzoyl hypochlorite from the reaction between silver benzoate and chlorine. We have found that benzoyl hypochlorite is formed as an unstable yellow oil when chlorine reacts with lithium benzoate in *NN*-dimethylformamide solution, as describd on p. 4496.

Attempts to initiate Vinyl Polymerization.—To obtain some evidence for the occurrence of reaction (2*a*) attempts were made to use lithium chloride–benzoyl peroxide mixtures in *NN*-dimethylformamide as initiators of vinyl polymerization. With styrene at a concentration of 2·5 mole $l.^{-1}$ no polymer was formed, although conditions were such that the maximum rate of radical formation was low enough to produce high polymers. This result is not surprising; as already stated the importance of the homolysis of the benzoyl hypochlorite is reduced in the presence of styrene, and, further, some of the hypochlorite may be removed by direct addition to the monomer. Acrylonitrile in *NN*-dimethylformamide solution was shown to react much less rapidly than styrene with chlorine and the hypochlorite, but this monomer could not be polymerized by the lithium chloride–benzoyl peroxide mixture, presumably because molecular chlorine is a powerful inhibitor of the polymerization of acrylonitrile.

These results, while providing no evidence that reaction (2*a*) participates in the decomposition, are consistent with the mechanism proposed.

The Reaction between Benzoyl Peroxide and Chloride in Dichloroethane Solution.—It was thought that some evidence for the formation of benzoyloxy-radicals might be obtained by using dichloroethane as solvent since this reacts less readily than *NN*-dimethylformamide with these radicals.[6] Tetraethylammonium chloride was used in place of lithium chloride, which is not soluble in dichloroethane.

The general features of the reaction under these conditions are very similar to those already described. (*a*) Chlorine is formed, and reaches its maximum concentration when the greater part of the peroxide has decomposed. The mixture becomes yellow, the colour being much deeper than that of an equivalent solution of chlorine in dichloroethane. The additional colour arises from the formation of tetraethylammonium trichloride, which was isolated as a yellow solid. This trichloride does not react at an appreciable rate with benzoyl peroxide. (*b*) The yield of chlorine is greater than 0·5 mole per mole of benzoyl peroxide decomposed. (*c*) One mole of benzoyl peroxide requires more than one mole of chloride for complete decomposition. These findings are consistent with the mechanism of reactions (1), (2), (3) as already described.

The reaction differs from that in *NN*-dimethylformamide in that appreciable quantities of carbon dioxide are formed, presumably by the decarboxylation:

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \longrightarrow \mathrm{Ph{\cdot}} + \mathrm{CO_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In *NN*-dimethylformamide this reaction cannot occur since the benzoyloxy-radicals are preferentially hydrogenated.[1] The yield of benzoyloxy-radicals would be expected to decrease with increasing initial chloride concentration, by virtue of reaction (3*a*); the yield of carbon dioxide should therefore decrease accordingly. Experiments at high, medium, and low [$\mathrm{Cl^-}$] were performed to test this; the molar yields of carbon dioxide based on the peroxide decomposed were 6·9%, 12·4%, 29·3% respectively. The yield of carbon dioxide thus shows the expected variation. Further, in the presence of styrene (initial concentration 0·17 mole $\mathrm{l.^{-1}}$) the yield is greatly reduced, to 2·6%. This would be the case if benzoyloxy-radicals react with styrene before the decomposition (6) can occur. However, according to Barson and Bevington's results,[7] concentrations of styrene as low as 0·2 mole $\mathrm{l.^{-1}}$ would not be expected to interfere significantly with reaction (6) in benzene solution, and if this is true in dichloroethane we are led to conclude that the low yield of carbon dioxide is not due to the scavenging of benzoyloxy-radicals by styrene. We believe that it is an indication of the reduced importance of reaction (2*a*) in the presence of styrene (cf. p. 4492); the direct addition of the hypochlorite to styrene may also be a contributory factor.

In the absence of olefins, 2-chloroethyl benzoate is a major product. This probably arises from interaction between benzoate ions and dichloroethane:

$$\mathrm{Ph{\cdot}CO{\cdot}O^-} + \mathrm{(CH_2Cl)_2} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}[CH_2]_2{\cdot}Cl} + \mathrm{Cl^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We have confirmed that a mixture of silver benzoate and tetraethylammonium chloride in dichloroethane rapidly yields the chloro-ester at 60°. Direct evidence of reaction (7) is also provided by measurements of chlorine and chloride concentrations. The total concentration in terms of equivalents of $\mathrm{Cl^-}$ was greater at the end of a run than at the start, showing that some chloride must have been derived from the solvent.

Related Reactions.—The reaction of benzoyl peroxide most closely analogous to (1) is

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[6] Bamford and White, unpublished results.

[7] Barson and Bevington, *J. Polymer Sci.*, 1956, **20**, 133.

the initial step in the decomposition accelerated by tertiary aromatic amines such as dimethylaniline. According to Horner and Schwenk [2] this follows the path:

$$\mathrm{Ph{\cdot}NMe_2 + (Ph{\cdot}CO{\cdot}O)_2 \longrightarrow [Ph{\cdot}\dot{N}Me_2]^+ + Ph{\cdot}CO{\cdot}O{\cdot} + Ph{\cdot}CO{\cdot}O^-} \quad . \ . \ . \ . \quad (8)$$

and thus differs from reaction (1) in leading to free radicals directly. However, both reactions (1) and (8) are nucleophilic displacements in which the driving force is derived from the electrophilic nature of the benzoyl peroxide molecule.

As already mentioned acyl hypohalites are intermediates in the Hunsdiecker reaction.[8] Homolysis of the hypohalite, followed by loss of carbon dioxide from the resulting acyloxy-radicals and subsequent recombination, give rise to the typical Hunsdiecker product—an alkyl or aryl halide. Such products were not encountered in the present work with *NN*-dimethylformamide as solvent. There appear to be two main reasons for this. First, in the presence of chloride, reaction (3*a*) gives the benzoate ion, and secondly, the benzoyloxy-radical participates readily in hydrogen transfer.[1] It is unlikely that Hunsdiecker products will be found in any solvent containing hydrogen atoms which are at all labile—hence the value of carbon tetrachloride as a reaction medium. In *NN*-dimethylformamide, for example, we have shown that the reaction between silver benzoate and bromine at −10° gives benzoic acid as the major product and not bromobenzene.

EXPERIMENTAL

Materials.—Benzoyl peroxide and *NN*-dimethylformamide were purified as described in Part I.[1] Tetraethylammonium chloride and lithium chloride were dried in a vacuum at 110° for several days. Dichloroethane was dried over barium oxide and distilled before use. Styrene was treated similarly after removal of stabilisers by washing with alkali.

Technique.—For studying reactions between benzoyl peroxide and chlorides ampoules having two limbs were used, into which solutions of the two reagents were separately pipetted in a dry box. The vessels were flushed with nitrogen, sealed, and allowed to reach thermal equilibrium in a thermostat before being shaken to mix the reactants. The contents were analysed after known intervals.

Analysis.—Peroxides were estimated iodometrically as in Part I.[1] In the presence of chlorine this method gives the sum of the chlorine and peroxide concentrations; the addition of styrene immediately before sampling removes chlorine and allows the peroxide alone to be titrated. Benzoyl hypochlorite, if present, will be estimated together with the chlorine; the concentrations of chlorine given in Fig. 2 may therefore be too high. The hypochlorite concentration is probably always very small and is, in any case, unlikely to be high enough to invalidate the conclusions drawn from Fig. 2.

In the presence of chlorine, chloride was estimated by converting the chlorine into chloride with sodium hydrogen sulphite and titrating the total chloride with silver nitrate to a potentiometric end-point. Alternatively, the chlorine was first removed with styrene and the chloride titrated directly.

Carbon dioxide was estimated as in Part I.[1]

Separation of Products.—After most of the *NN*-dimethylformamide had been removed by distillation in a vacuum, lithium benzoate and benzoic acid were isolated by extraction with 5% aqueous sodium carbonate after addition of ether. Benzoic acid, precipitated from the alkaline extract with acid, was collected, dried, and weighed. *N*-Benzoyloxymethyl-*N*-methylformamide contained in the ether extract was obtained as a viscous colourless oil, n_D^{20} 1·5398 (lit.,[1] 1·5401), by distillation in a molecular still (Found: C, 63·0; H, 5·9; N, 7·3. Calc. for $C_{10}H_{11}O_3N$: C, 62·2; H, 5·7; N, 7·3%).

Isolation of 2-*Chloroethyl Benzoate.*—Benzoyl peroxide (2·7 g.) was allowed to react with tetraethylammonium chloride (3·4 g.) in dry dichloroethane (50 ml.) at 60° under nitrogen. After 90 min. a liquid containing the ester was isolated by the procedure described above for *N*-benzoyloxymethyl-*N*-methylformamide and distilled in a vacuum. The fraction of b. p. 137°/14 mm., $n_D^{18\cdot5}$ 1·5311, was collected (Found: C, 58·1; H, 5·0; Cl, 20·4. Calc. for $C_9H_9ClO_2$: C, 58·5; H, 4·9; Cl, 19·3%). The same product was obtained by warming a mixture of silver

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[8] Johnson and Ingham, *Chem. Rev.*, 1956, **56**, 219.

benzoate and tetraethylammonium chloride with dichloroethane. (Analogous reactions between other silver salts and other halogenated solvents in the presence of tetraethylammonium chloride gave corresponding products.) A synthetic sample of 2-chloroethyl benzoate prepared from ethylene chlorohydrin and benzoyl chloride distilled at 137°/14 mm. and had $n_D^{18\cdot5}$ 1·5310. Retention times for the three samples in a gas-chromatography apparatus with a Silicone-impregnated Celite column at 186° were identical.

Reaction of Chlorine with Lithium and Silver Benzoates in NN-*Dimethylformamide.*—*NN*-Dimethylformamide (50 ml.) saturated with chlorine was allowed to react with solid lithium benzoate (10 g.) at 10°. Pouring the mixture into water at 0° then caused a yellow oil to separate; this rapidly decomposed into benzoic acid and chlorine at room temperature. It reacted at once with cyclohexene to give a mixture of 1,2-dichlorocyclohexane and 2-chlorocyclohexyl benzoate, the latter being identified by its hydrolysis to *trans*-cyclohexane-1,2-diol (m. p. 104°) and benzoic acid. The benzoyl hypochlorite could not be obtained pure.

Attempts were made to prepare chlorobenzene by the Hunsdiecker reaction in *NN*-dimethylformamide from silver benzoate and chlorine at −10° for periods up to 15 hr. No chlorobenzene could be detected by gas chromatography. After filtration and removal of the solvent by distillation at room temperature benzoic acid remained.

Yields of Carbon Dioxide.—Carbon dioxide evolved in the reaction of tetraethylammonium chloride and benzoyl peroxide in dichloroethane at 60° was measured at different chloride concentrations. At very high chloride concentrations, achieved by adding 0·004 mole of peroxide in 25 ml. of dichloroethane to 0·02 mole of chloride in 25 ml. of dichloroethane, the yield of carbon dioxide was 6·9 mole %. Low chloride concentrations, obtained by adding 0·012 mole of the chloride in 25 ml. of solvent dropwise in 6 hr. to 0·0046 mole of peroxide in 25 ml. of dichloroethane, gave 29·3 mole % of carbon dioxide. From 0·004 mole of peroxide and 0·011 mole of chloride in 50 ml. of dichloroethane, the yield of carbon dioxide was 12·4%. Addition of 0·0087 mole of styrene to this reduced the yield to 2·6 moles %.

Polymerization Experiments.—Reactions between benzoyl peroxide and tetraethylammonium or lithium chlorides were carried out in dichloroethane or *NN*-dimethylformamide solution containing 2·5 mole $l.^{-1}$ of acrylonitrile or styrene. Before reaction the chloride and peroxide solutions contained in separate side-arms attached to a dilatometer were thoroughly degassed, mixed, and allowed to react at 40°. No contraction was observed, indicating that no polymerization had occurred. No polymer could be precipitated from the solution at the end of the experiment.

The inhibiting effect of chlorine on the polymerization of acrylonitrile was demonstrated by heating a solution of chlorine in acrylonitrile containing 1% of benzoyl peroxide under nitrogen at 60°. No precipitation of polymer occurred so long as the yellow colour of chlorine persisted. Addition of one drop of styrene, which reacts rapidly with chlorine, was followed by the formation and precipitation of polymer. In a control experiment without chlorine, polymer became visible almost immediately.

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