meric catalysts may have considerable synthetic utility for the synthesis of chemical compounds in the absence of water or highly acidic or basic groups; at present, 2-pyridone, an extremely weak acid and base, is the preferred catalyst for such applications.[50,51]

Acknowledgments. The author gratefully acknowledges many stimulating discussions with Professor Jack Halpern.

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(50) H. T. Openshaw and N. Whittaker, *J. Chem. Soc., C,* 89 (1969).

(51) Note Added in Proof. Additional references on the subject of bifunctional (and possibly tautomeric) catalysis include the papers of Blackburn and Jencks,[52] Glutz and Zollinger,[53] Nakamizo,[54] and Litvinenko and Oleinik (and references therein[55]). Bitter and Zollinger observed that acetic acid was a more effective catalyst than trichloroacetic acid for the reaction of cyanuric chloride with aniline in nonpolar solvents.[56]

(52) G. M. Blackburn and W. P. Jencks, *J. Amer. Chem. Soc.,* **90,** 2638 (1968).

(53) B. Glutz and H. Zollinger, *Angew. Chem. Intern. Ed. Engl.,* 4, 440 (1965).

(54) N. Nakamizo, *Bull. Chem. Soc. Japan,* 42, 32, 1071, 1078 (1969).

(55) L. M. Litvinenko and N. M. Oleinik, *Ukr. Khim. Zh.,* 174 (1966).

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Benzoyl Hypochlorite, an Intermediate in the Oxidation of Ionic Chlorides and Hydrogen Chloride by Benzoyl Peroxide[1]

N. J. Bunce[2] and Dennis D. Tanner

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. *Received May 19, 1969*

Abstract: The oxidation of chloride ion by benzoyl peroxide yields benzoyl hypochlorite. Free-radical initiation causes the decomposition of this intermediate to chlorobenzene, and in this and other reactions, the intermediate shows the same chemistry as the intermediate in the Hunsdiecker reaction. In the presence of an alkane, the acyl hypochlorite functions as a free-radical chlorinating reagent. Investigation of the mechanism of this reaction suggests that atomic chlorine is the chain-carrying species. When hydrogen chloride is oxidized by benzoyl peroxide in the absence of an alkane, only traces of chlorobenzene are produced. This is attributed to the rapid reaction of hydrogen chloride with the acyl hypochlorite to give molecular chlorine. In the presence of an added hydrocarbon, the chlorine so formed yields alkyl chlorides by a free-radical process, the mechanism of which is complicated by the reversible reaction of the intermediate alkyl radicals with the hydrogen chloride in the system.

In a previous paper,[3] we reported the mechanism of the free-radical reaction of cyanogen chloride with alkanes. Photochemical initiation of the reaction led to the formation of alkyl cyanides as the exclusive products (eq 1), but promotion with benzoyl peroxide gave alkyl chlorides in addition.

$$\mathrm{ClCN + RH \xrightarrow{h\nu} RCN + HCl} \qquad (1)$$

The alkyl chlorides were shown to be produced through the reaction of benzoyl peroxide with hydrogen chloride, the by-product of alkyl cyanide formation. In the presence of cyclohexane, acetonitrile solutions of hydrogen chloride could be oxidized to produce ultimately cyclohexyl chloride almost quantitatively (eq 2).

$$\mathrm{HCl + (PhCO_2)_2 + RH \longrightarrow RCl + 2PhCO_2H} \qquad (2)$$

Previously, Bamford and White[4] had studied the reaction between ionic chlorides and benzoyl peroxide in dimethylformamide solution. The reaction was much faster than the thermal decomposition of benzoyl peroxide, and was first order in each reactant. It was concluded that free radicals were not involved in the reaction, and benzoyl hypochlorite (I) was proposed as the first formed intermediate (eq 3).

$$\mathrm{(PhCO_2)_2 + LiCl \longrightarrow PhCO_2Li + PhCO_2Cl} \qquad (3)$$

More recently, Kochi, Graybill, and Kurz[5] have also studied this reaction. In the presence of added arenes they obtained very high yields of ring-chlorinated products, and it was proposed that benzoyl hypochlorite was the chlorinating agent. When the arene carried an alkyl side chain, a competing free-radical chain chlorination of the side chain occurred; cyclohexane exhibited similar behavior.

Acyl hypohalites have also been proposed as the intermediates in the Hunsdiecker reaction,[6a] the currently accepted mechanism of which[6b] is shown in eq 4a–4d.

$$\mathrm{RCO_2Ag + X_2 \longrightarrow AgX + RCO_2X} \qquad (4a)$$

$$\mathrm{RCO_2X \longrightarrow RCO_2\cdot + X\cdot} \qquad (4b)$$

$$\mathrm{RCO_2\cdot \longrightarrow R\cdot + CO_2} \qquad (4c)$$

$$\mathrm{R\cdot + RCO_2X \longrightarrow RX + RCO_2\cdot} \qquad (4d)$$

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(1) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) Killam Memorial Postdoctoral Fellow, University of Alberta, 1967–1969.

(3) D. D. Tanner and N. J. Bunce, *J. Am. Chem. Soc.,* **91,** 3028 (1969).

(4) C. H. Bamford and E. F. T. White, *J. Chem. Soc.,* 4490 (1960).

(5) J. K. Kochi, B. M. Graybill, and M. Kurz, *J. Am. Chem. Soc.,* **86,** 5257 (1964).

(6) (a) W. Bockemüller and F. W. Hoffman, *Ann.,* **519,** 165 (1935); (b) C. V. Wilson, "Organic Reactions," Vol. 9, John Wiley & Sons, New York, N. Y., 1957, p 332, and references cited therein.

Similarly, acyl hypoiodites have been indicated to be intermediates in the decomposition of benzoyl peroxides in the presence of iodine.[7]

Since these reactions are proposed to proceed through a common intermediate, it would be expected that chlorobenzene, the "Hunsdiecker product," should be formed in the reaction between chloride ion and benzoyl peroxide. Bamford and White were unable to find any chlorobenzene in their reactions, and concluded that the reactive intermediate preferentially attacked the solvent. However, Kochi and his coworkers were able to observe this product in the less reactive solvent, acetic acid.

A number of other reagents are known to undergo a polar reaction with benzoyl and other peroxides. The reaction of iodide ion with peroxides in the basis of their iodometric determination;[8] polar processes have been shown to be important also in the reaction of amines and phenols[9-11] with benzoyl peroxide.

The purpose of the present study has been to obtain further evidence for the intermediacy of benzoyl hypochlorite in the benzoyl peroxide oxidations of hydrogen chloride and ionic chlorides, and to determine the mechanism of free-radical chlorination of alkanes by this reagent. We have approached the problem by seeking parallels between the behavior of the benzyol peroxide/chloride ion reagent and the Hunsdiecker reaction, both of which have been postulated as involving acyl hypohalites as intermediates.

Results and Discussion

Oxidation of Chloride Ion in the Absence of Added Alkanes. In the first series of experiments, a solution of tetraethylammonium chloride in acetonitrile was oxidized at 98° with varying quantities of benzoyl peroxide. In this very unreactive solvent chlorobenzene, the "Hunsdiecker product" was formed, the optimum yield being 50%; see Figure 1.

As in the case of the Hunsdiecker reaction, this product formed only when all the reagents were carefully dried; the addition of 1% water to the solvent almost completely suppressed the formation of chlorobenzene.

In order to ascertain the fate of the remaining 50% of the material, the acidic portion was analyzed for chlorinated benzoic acids. *m*-Bromobenzoic acid has, for example, been isolated from the Hunsdiecker reaction of bromine with silver benzoate.[12] In our system we were unable to find evidence for the formation of chlorinated benzoic acids when acetonitrile was the solvent, since it appeared that a reaction with the solvent took place preferentially. When equivalent quantities of benzoyl peroxide and tetraethylammonium chloride reacted in carbon tetrachloride solution, the three isomeric chlorinated benzoic acids (15%) were produced, as well as chlorobenzene (30%).

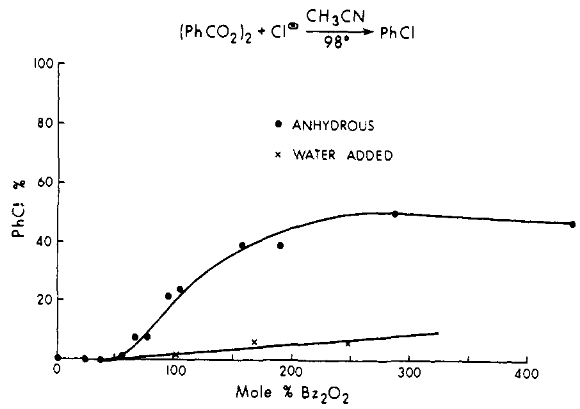

Figure 1. The reaction of chloride ion with benzoyl peroxide in acetonitrile at 98°.

Production of chlorinated benzoic acids is analogous to the electrophilic chlorination of arenes by the presumed benzoyl hypochlorite studied by Kochi, Graybill, and Kurz.[5] In agreement with their results we observed that when anisole was added to the benzoyl peroxide/chloride ion reagent in solvent carbon tetrachloride, *p*-chloroanisole was the only chlorinated product. Likewise in the halogen/silver salt reaction, addition of an arene leads to its electrophilic halogenation.[13] Electrophilic chlorination of arenes is also effected by alkyl hypochlorites.[14]

The reaction of a halogen with a silver salt in the presence of an olefin (Prevost reaction) results in the addition of the elements of the acyl hypohalite across the double bond of the alkene.[6a,15] Similarly, the oxidation of tetraethylammonium chloride with an equimolar quantity of benzoyl peroxide, using cyclohexene as the solvent, gave the addition products of chlorine (*trans*-1,2-dichlorocyclohexane) and of benzoyl hypochlorite (2-chlorocyclohexyl benzoate) to cyclohexene in yields of 27 and 34%, respectively. 2-Chlorocyclohexyl benzoate was shown not to arise through the addition of chlorine to cyclohexene in the presence of benzoate anions; the addition of a solution of chlorine in carbon tetrachloride to a mixture of cyclohexene and a large excess of sodium benzoate gave only the dichloride, and no chlorobenzoate.

The above experiments, showing the decomposition of benzoyl hypochlorite to chlorobenzene, and its reactions with aromatic compounds and olefins, establish reasonably securely that common intermediates are formed in the oxidation of chloride ion with benzoyl peroxide and in the reaction of halogens with silver carboxylates.

Oxidation of Chloride Ion in the Presence of Alkanes. When tetraethylammonium chloride was oxidized by benzoyl peroxide in acetonitrile at 98° in the presence of added alkanes, alkyl chlorides were produced. When 2,3-dimethylbutane was the substrate, the results shown in Figure 2 were obtained.

The optimum yield of alkyl chlorides (total of both isomers) was about 60% and a smaller quantity of

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[7] G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

[8] (a) G. Tsuchihashi, S. Miyajima, T. Otsu, and O. Simamura, *Tetrahedron*, **21**, 1039, 1049 (1965); (b) V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941); (c) K. Nozaki, *Anal. Chem.*, **18**, 583 (1946).

[9] C. Walling and N. Indictor, *J. Am. Chem. Soc.*, **80**, 5814 (1958).

[10] C. Walling and R. B. Hodgson, *ibid.*, **80**, 228 (1958).

[11] C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 590–596.

[12] L. G. S. Brooker and S. Smiles, *J. Chem. Soc.*, 1723 (1926); *cf.* ref 13.

[13] (a) D. Papa, E. Schwenk, and E. Klingsberg, *J. Am. Chem. Soc.*, 72, 2623 (1950); (b) W. G. Dauben and H. Tilles, *ibid.*, 72, 3185 (1950); (c) R. A. Barnes and R. J. Prochaska, *ibid.*, 72, 3188 (1950); (d) M. Sletzinger and C. R. Dawson, *J. Org. Chem.*, **14**, **670** (1949); (e) L. Birchenbach and J. Goubeau, *Ber.*, **66**, 1280 (1933); (f) ref 3b, pp 340–341.

[14] M. Anbar and D. Ginsburg [*Chem. Rev.*, **54**, 925 (1954)] cite examples of the reactions of alkyl hypohalites with arenes and alkenes.

[15] (a) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 6256 (1957), and references cited therein; (b) ref 6b, pp 339–340.

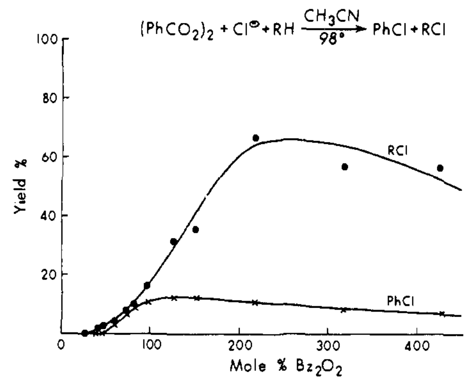

Figure 2. The reaction of chloride ion with benzoyl peroxide and 2,3-dimethylbutane in acetonitrile at 98°.

chlorobenzene was also formed. A point of interest in these results is that, like those obtained in the absence of hydrocarbon (Figure 1), no products are formed when the initial concentration of benzoyl peroxide is very low. Under these conditions, the intermediate benzoyl hypochlorite yields chlorobenzene (or in the presence of alkanes, alkyl chlorides) only when moderate or large quantities of benzoyl peroxide are present.

These results imply that at these temperatures, benzoyl hypochlorite is sufficiently stable toward homolytic decomposition that other processes can compete favorably with free-radical decomposition. Only under conditions where the concentration of benzoyl peroxide is sufficiently large that high concentrations of radicals are present in the solution do the free-radical products (chlorobenzene or alkyl chlorides) form in preference. This is consistent with the findings of Kochi, Graybill, and Kurz,[5] who observed nearly quantitative electrophilic chlorination of anisole from the reaction of benzoyl peroxide with excess lithium chloride at 65°. Furthermore, Bamford and White[4] found that in dimethylformamide at 60° mixtures of benzoyl peroxide and excess chloride ion did not cause polymerization of added styrene. They reasoned therefore that free radicals were not produced in the reaction, in contrast to the analogous reaction between benzoyl peroxide and dimethylaniline which apparently leads directly[16] or nearly so[9] to free radicals.

In our studies, we have confirmed that no polymerization of added styrene occurs at 98° when chloride ion is in large excess, but when the benzoyl peroxide is in excess (the region of the curves in Figures 1 and 2 where products are formed) addition of styrene to the reaction mixture causes polymerization (see Table I). We also observed that chlorinated products only form in those mixtures where benzene is also a product, and that product yield increases with increasing benzene formation, suggesting that phenyl radicals formed in the thermal decomposition of benzoyl peroxide may function as free-radical chain initiators. At very low concentrations of benzoyl peroxide, the rapid reaction with chloride ion consumes all the benzoyl peroxide so that none is available for initiating free-radical chains through thermal decomposition.

Table I. Polymerization of Styrene in Acetonitrile at 98° by the Benzoyl Peroxide/Chloride Ion Reagent[a]

Peroxide, mmoles	$(C_2H_5)_4N^+Cl^-$, mmoles	Weight of polymer,[b] g
0.0	0.0	0.21
1.03	0.0	6.82
1.03	0.61	4.32
1.02	6.06	0.19

[a] A 1:1 mixture of styrene and acetonitrile (30 ml) was heated to 98° for 1 hr. [b] After precipitation with methanol.

Nevertheless, although benzoyl hypochlorite does not yield free-radical products except in the presence of high concentrations of benzoyl peroxide it appears to be consumed by other processes if this initiator is not available. In acetonitrile solution we believe that the hypochlorite reacts with the solvent, possibly by addition to the triple bond,[17] although attempts to isolate any addition products by evaporation of the solvent from the reaction mixtures were unsuccessful and only tars resulted.

The use of 2,3-dimethylbutane as the hydrocarbon substrate gave rise to two isomeric alkyl chlorides, and the ratio of these products allowed the selectivity of the hydrogen atom abstracting species to be determined. At benzoyl peroxide:chloride ion ratios of less than unity, the primary:tertiary selectivity per hydrogen was 1:5 ± 0.5, but as the proportion of benzoyl peroxide increased the selectivity became gradually larger, until when the benzoyl peroxide was present in threefold excess, a selectivity of 1:13 was observed (see Experimental Section, Table IV). Noting that at high benzoyl peroxide concentrations much peroxide decomposes thermally to phenyl radicals and thence benzene, we believe that the greater numbers of phenyl radicals at the higher peroxide concentrations account for a substantial proportion of the hydrogen abstraction, and thus impose their selectivity on the over-all abstraction process. At moderate benzoyl peroxide concentrations very little benzene is produced, so that 1:5 may be taken to represent the primary:tertiary selectivity of the chloride ion/benzoyl peroxide reagent.

These selectivity data are also parallelled in the Hunsdiecker reaction. Filtration of a solution of chlorine mixed with excess silver benzoate into 2,3-dimethylbutane followed by illumination of the resulting solution caused the isomeric alkyl chlorides to be formed with a primary:tertiary selectivity per hydrogen of 1:4 ± 0.5.

Determination of the selectivity of the hydrogen abstracting agent allows a distinction to be drawn between different free-radical chain chlorination processes, illustrated by Schemes I, II, and III.

Scheme I

$$PhCO_2\cdot \longrightarrow Ph\cdot + CO_2$$
$$Ph\cdot + RH \longrightarrow PhH + R\cdot$$
$$R\cdot + PhCO_2Cl \longrightarrow RCl + PhCO_2\cdot$$

Scheme II

$$PhCO_2\cdot + RH \longrightarrow PhCO_2H + R\cdot$$
$$R\cdot + PhCO_2Cl \longrightarrow RCl + PhCO_2\cdot$$

Scheme III

$$RH + Cl\cdot \longrightarrow R\cdot + HCl$$
$$HCl + PhCO_2Cl \longrightarrow Cl_2 + PhCO_2H$$
$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$$

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[16] L. Horner and E. Schwenk, *Angew. Chem.*, **61**, 411 (1949).

[17] *Cf.* the addition of acyl hypochlorites to acetylenes: C. Prévost and J. Weinman, *Compt. Rend.*, 204, 700, 989 (1937).

Scheme I may be rejected immediately because it does not take account of the fact that *two* molecules of benzoate are formed for every chloride ion oxidized. Furthermore, the selectivity should be that of the phenyl radical,[18] *viz.* 1:44, whereas 1:5 is the observed value.

Scheme II is analogous to the mechanism of chlorination by *t*-butyl hypochlorite[19] in which abstraction is by way of the *t*-butoxy radical. The case against this mechanism is that the benzoyloxy radical, proposed as the hydrogen abstracting reagent, is known to decarboxylate very rapidly to the phenyl radical, giving benzene as the major product rather than benzoic acid.[20] Furthermore, the resonance-stabilized benzoyloxy radical would be expected to be more selective than an alkoxy radical, but yet hydrogen abstraction in the present reaction is a less, not more selective process than abstraction by an alkoxy (*e.g.*, *t*-butoxy[21]) radical.

Scheme III is analogous to the mechanism of chlorination of alkanes by *N*-chlorosuccinimide, proposed by Goldfinger.[22] Similar processes have been observed more recently in the chlorination of substituted toluenes by *t*-butyl hypochlorite.[23] Scheme III accounts for all the experimental data, in that it explains the production of benzoic acid, and in that the observed primary:tertiary selectivity (1:5) is the same as that reported by Russell[24] for abstraction by atomic chlorine. We therefore propose Scheme III as the mode of chlorination of alkanes by the chloride ion/benzoyl peroxide reagent. This sequence of reactions requires that the reaction of hydrogen chloride with benzoyl hypochlorite be very rapid, and this is consistent with the known instability of alkyl hypochlorites[25] and N-chloroamines[26] toward hydrogen chloride. Indeed, it is the reactivity of positive halogen compounds with hydrogen halides that gives, for example, NBS its application as a reagent capable of maintaining a constant low concentration of bromine in solution. Conversely it seems that the reaction of chloride ions with benzoyl hypochlorite must be relatively slow, because when equimolar quantities of tetraethylammonium chloride and benzoyl peroxide interact in acetonitrile, all the benzoyl peroxide is consumed according to eq 3. If the reaction of chloride ion with the intermediate were fast then we would observe the stoichiometry of eq 5.

$$2Cl^- + (PhCO_2)_2 \longrightarrow Cl_2 + 2PhCO_2^- \qquad (5)$$

Oxidation of Hydrogen Chloride. It would be anticipated that the rapid reaction of hydrogen chloride with benzoyl hypochlorite would influence the course of oxidation of hydrogen chloride with benzoyl peroxide, and this was found to be so.

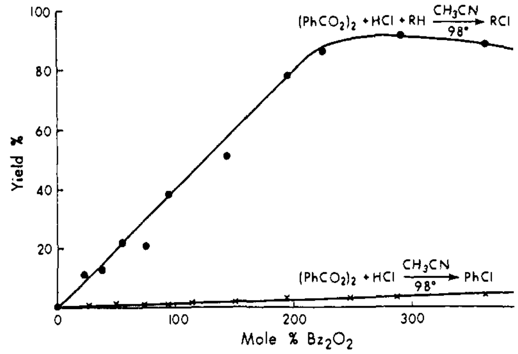

Figure 3. The oxidation of hydrogen chloride with benzoyl peroxide in acetonitrile at 98°.

As shown in Figure 3, oxidation of hydrogen chloride in the absence of a hydrocarbon affords no more than traces of chlorobenzene, no matter how large the initial concentration of benzoyl peroxide. This is interpreted as being due to the reaction of hydrogen chloride with the intermediate acyl hypochlorite being much faster than its reaction with benzoyl peroxide (*i.e.*, $k_7 > k_6$).

$$HCl + (PhCO_2)_2 \xrightarrow{k_6} PhCO_2H + PhCO_2Cl \qquad (6)$$

$$PhCO_2Cl + HCl \xrightarrow{k_7} PhCO_2H + Cl_2 \qquad (7)$$

Consequently the quantity of benzoyl hypochlorite which is available for decomposition to chlorobenzene is always small, even at large initial concentrations of peroxide.

When hydrogen chloride was oxidized with varying quantities of benzoyl peroxide in the presence of cyclohexane, under optimum conditions an almost quantitative yield of cyclohexyl chloride was obtained.[3] No chlorobenzene was produced. In Figure 3 is presented a similar set of experiments with 2,3-dimethylbutane. Since it is proposed that the reaction of benzoyl hypochlorite with hydrogen chloride to give chlorine is very rapid, it would be anticipated that the distribution of isomeric chlorides would reflect the selectivity of hydrogen abstraction by chlorine atoms as in Scheme III above. Unexpectedly, this was found not to be the case; both *n*-butane and 2,3-dimethylbutane (and/or isobutane) were chlorinated extremely selectively (see Table II), and the selectivity varied with the proportion of hydrogen chloride in the reaction mixture.

Table II. Comparison of the Selectivity of Hydrogen Atom Abstraction by the Hydrogen Chloride/Benzoyl Peroxide Reagent with That of Chlorine

Mole % benzoyl peroxide	*S/P* (*n*-butane)[a]	*T/P* (isobutane)[a]
0.3	400	12,000
3.5	60	900
Cf. Cl_2	3.6	4.1[b]

[a] Per hydrogen atom. [b] 2,3-Dimethylbutane.

The unexpectedly high selectivity caused us to consider whether the reversible reaction of alkyl radicals with hydrogen chloride might be occurring (illustrated in Scheme IV). A similar sequence of reactions has

Scheme IV

$$R\cdot + Cl_2 \xrightarrow{k_8} RCl + Cl\cdot \qquad (8)$$

$$Cl\cdot + RH \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} R\cdot(\text{primary}) + HCl \qquad (9)$$

$$Cl\cdot + RH \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} R\cdot(\text{secondary}) + HCl \qquad (10)$$

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(18) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(19) (a) C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967); (b) D. J. Carlsson and K. U. Ingold, *ibid.*, **89**, 4885, 4891 (1967).

(20) Decomposition of benzoyl peroxide (4 g) in 60 ml of cyclohexane heated to reflux gave <1% benzoic acid; *cf.* ref 11, pp 474–491.

(21) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(22) J. Adam, P. A. Gosselain, and P. Goldfinger, *Bull. Soc. Chim. Belges*, **65**, 533 (1956).

(23) C. Walling and J. A. McGuinness, *J. Am. Chem. Soc.*, **91**, 2053 (1969).

(24) G. A. Russell, *ibid.*, **80**, 4987 4997 (1958).

(25) M. Anbar and J. Dostrovsky, *J. Chem. Soc.*, 1094 (1954).

(26) D. D. Tanner and M. W. Mosher, *Can. J. Chem.*, 47, 715 (1969).

Table III. The Oxidation of Deuterium Chloride by Benzoyl Peroxide in Acetonitrile at 98° in the Presence of Added Alkanes

DCl, mmoles	Peroxide, mmoles	RH, mmoles	Total vol, ml	PhCl, mmoles	RCl, mmoles	RD,[a] mg-atom	RD/RCl
0.70	0.70	0.78[b]	1.1	0.0088	0.0339[d]	0.24	7.1
0.70	0.70	0.78[b]	1.1	0.0061	0.0519[d]	0.17	3.3
0.60	0.58	0.93[c]	1.1	0.0114	0.119[e]	0.43	2.8
0.60	0.58	0.93[c]	1.1	0.0097	0.117[e]	0.31	3.4

[a] Including polydeuteration. [b] 2,3-Dimethylbutane. [c] Cyclohexane. [d] 2-Chloro-2,3-dimethylbutane. [e] Chlorocyclohexane.

previously been observed in the cyanation reaction of cyanogen chloride.[3]

Since chlorine atoms abstract secondary (or tertiary) hydrogens more rapidly than primary ones, then $k_{10} > k_9$. From known bond energy data[27] and from the kinetics of the gas phase chlorination of alkanes[28] it may be deduced that the reaction of a primary radical with hydrogen chloride is faster than that of a secondary (or tertiary) radical, *i.e.*, $k_{-9} > k_{-10}$. The result of imposing these inequalities upon equilibria 9 and 10 is to increase the stock of secondary (or tertiary) radicals at the expense of the primary radicals, giving an increase in the observed apparent selectivity. This selectivity is then not the same as the selectivity of the abstracting species in the absence of reversibility.[29]

In order to determine whether this hypothesis was correct, solutions of deuterium chloride were oxidized by benzoyl peroxide in the presence of alkanes, and the unreacted hydrocarbon was analyzed for incorporation of deuterium by high-resolution mass spectrometry. The results of experiments with 2,3-dimethylbutane and cyclohexane as substrates are given in Table III. It can be seen that the reversible reaction of alkyl radicals with hydrogen chloride is a major process in these systems, for between three and seven acts of incorporation took place for every molecule of alkyl chloride formed. These values are lower limits upon the extent of the exchange reaction, for in the course of the reaction, the deuterium chloride is progressively diluted with hydrogen chloride.

Since chlorinations of alkanes with molecular chlorine do not exhibit the reversibility phenomenon, it is necessary to inquire why it is observed in the reaction under study. The product-forming reaction (eq 8) is in competition with the reaction of alkyl radicals with hydrogen chloride (reverse of eq 9 and eq 10). Normally in chlorinations there is an abundant supply of chlorine molecules and the faster, exothermic process (8) dominates. In the present example the supply of chlorine is limited by the rate-determining process (6), since $k_7 > k_6$; chlorine is therefore probably used up as fast as it is formed, so that its concentration is always very low. Consequently, an alkyl radical is able to react with hydrogen chloride before it encounters a chlorine molecule with which to chain transfer. We propose that Scheme IV represents the mechanism of chlorination of the hydrogen chloride/benzoyl peroxide reagent, and that hydrogen atom abstraction is by way of atomic chlorine, despite the observed selectivity data of Table II.

Experimental Section

Materials. The hydrocarbons, *n*-butane, isobutane, cyclohexane, cyclohexene, and 2,3-dimethylbutane were Phillips Research Grade and were used without purification.

Acetonitrile was obtained from J. T. Baker Chemical Co., and was dried by standing over activated molecular sieve for 2 days and distilled before use when necessary.

Molecular sieve (Linde, Union Carbide Corp.) was activated by heating for 1 hr in an open flask using a semiluminous Bunsen flame.

Deuterium chloride (Merck, Sharp and Dohme (Canada) Ltd.) (99.5%) was used as supplied.

Benzoyl peroxide (Fisher Scientific Co.) was used as supplied (purity by iodometric titration >98%).

Styrene was from Eastman Organic Chemicals and was distilled before use.

Analytical. Solutions of hydrogen chloride and chloride ion in acetonitrile were estimated by titration against standard alkali and by Mohr's method, respectively. Chloride ion was estimated in the presence of benzoate by prior acidification with nitric acid. Positive halogen compounds were estimated iodometrically.

Glpc Analysis. Acid washed Chromosorb W was used as a glpc support through this work. Quantitative analyses were carried out using an Aerograph "Hy-Fi" Model 600 D gas chromatograph equipped with flame-ionization detector and 10 ft × $^1/_8$ in. stainless steel columns. Products were estimated by comparing their peak areas with those of an added standard, after calibration of the response of the instrument with authentic materials in the usual way.[30] Products were collected from an Aergoraph Model 202 gas chromatograph equipped with a thermal conductivity detector and 10 ft × 0.25 in. stainless steel columns. The products were identified by comparing their ir spectra with those of authentic samples, in conjunction with comparison of their glpc retention times, unless otherwise indicated. Yields are based on initial molar quantity of chloride ion or hydrogen chloride.

Mass Spectra. For deuteration studies, mass spectra were run on an AEI Model MS9 as described previously.[3]

When gas chromatography was carried out coupled directly to the mass spectrometer. (gc/mass spectroscopy) the instrument used was an AEI Model MS12 in conjunction with an Aerograph "Hy-Fi" Model III gas chromatograph. Routine analyses were run on an AEI Model MS2.

Procedure. Reactions were conducted in sealed, evacuated, Pyrex ampoules which were allowed to stand in a constant-temperature bath for an appropriate period in the dark, unless stated otherwise. They were opened after being cooled at 77°K, and their contents were analyzed by glpc. Samples of the products were collected by preparative glpc and their ir spectra compared with those of authentic materials.

Reaction of Tetraethylammonium Chloride with Benzoyl Peroxide. (i). To aliquots of a 0.38 *M* solution of tetraethylammonium chloride in dry acetonitrile (1.0 ml) was added benzoyl peroxide in quantities ranging from 0.14 to 1.68 mmoles. The sealed degassed ampoules were heated to 98° for 1 hr, and after opening, a known quantity of bromobenzene was added to each as a standard for the glpc analysis (SE30, 85°). The results of these experiments are illustrated in Figure 1. In four similar experiments where the quantity of benzoyl peroxide varied between 0.40 and 0.94 mmoles, water (1%) was added to the solvent. The results of these experiments are also found in Figure 1. Comparison of glpc retention times of the components of the mixture with authentic benzoic acid and the three chlorinated benzoic acids (Carbowax 20M, 240°) or comparison of their methyl esters after treatment with diazo-

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(27) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(28) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 11 (1965).

(29) This point is discussed more fully in ref 3.

(30) D. D. Tanner and P. B. Van Bostelen, *J. Org. Chem.*, **32**, 1517 (1967).

methane (dinonyl phthalate (DNP) 140° or diisodecyl phthalate (DIDP), 150°)[31] indicated that only benzoic acid was present.

ii. A mixture of benzoyl peroxide (5.0 g, 21 mmoles), tetraethylammonium chloride (3.0 g, 18 mmoles), and cyclohexane (50 ml) was stirred in the dark at room temperature (25 ± 3°) for 150 hr. After the reaction 97% of the benzoyl peroxide had been consumed, while in a control reaction without tetraethylammonium chloride, less than 10% had decomposed. Analysis by glpc of the solution (SE30, 85°) with bromobenzene as an added standard indicated that cyclohexyl chloride (15%) had been formed. The reaction mixture was extracted with base, and the aqueous phase acidified, extracted into ether, and treated with diazomethane. Analysis by glpc (DNP, 140°) showed the presence of the chlorinated methyl benzoates in a total yield of 11%. Gc/mass spectroscopy (DNP, 140°) confirmed that the compounds were the three chlorinated esters, and comparison of retention times with authentic materials gave the elution order *para*, *meta*, *ortho*. The isomer ratio *ortho*:*meta*:*para* was 21:15:64.

iii. The experiment was repeated using the same quantities of reactants, but with carbon tetrachloride as the solvent. An analogous analytical procedure indicated that the products were chlorobenzene (30%) and the isomeric chlorobenzoic acids (15%, as methyl esters).

iv. When the reaction using carbon tetrachloride as solvent was repeated in the presence of anisole (10 g, 93 mmoles), no chlorinated benzoic acids were formed. *p*-Chloroanisole was identified by glpc (DIDP and SE30, 150°) as the only identifiable chlorinated material (25%) and this was confirmed by isolation of the substance (ir, nmr).

Reaction of Tetraethylammonium Chloride with Benzoyl Peroxide in Cyclohexene. A mixture of benzoyl peroxide (5.0 g, 21 mmoles), tetraethylammonium chloride (3.0 g, 18 mmoles), and cyclohexene (50 ml) was stirred in the dark at room temperature for 100 hr. The benzoyl peroxide was completely consumed in the reaction, while a control experiment showed <10% peroxide decomposition when no chloride was added. Glpc analysis (SE30, 50° programmed at 5°/min to 220°) showed two large and one smaller peak. Gc/mass spectroscopy (SE30, same program) analysis of these three compounds showed they had the same mass spectra as dichlorocyclohexane, cyclohexyl benzoate (minor component <1%) and 2-chlorocyclohexyl benzoate (see below). The reaction mixture was concentrated and chromatographed on silica gel (120 g). Benzene (125 ml) eluted 1,2-dichlorocyclohexane (ir and nmr spectra identical with authentic material, 27%). Ether (1%) in benzene (600 ml) eluted 2-chlorocyclohexyl benzoate (34%, ir and nmr spectra identical with authentic material, see below). The reaction was repeated at 50°, with a reaction time of 2 hr. The results were similar.

***cis*- and *trans*-2-Chlorocyclohexyl Benzoate.** Equimolar (0.05 *M*) quantities of benzoyl chloride, 2-chlorocyclohexanol (commercial mixture of isomers), and pyridine were heated to reflux for 2 hr in benzene (40 ml). The cooled reaction mixture was filtered to remove pyridinium hydrochloride, and, after evaporation of the solvent, was distilled under reduced pressure to give *cis*- and *trans*-2-chlorocyclohexyl benzoate (10 g, 83%): ir (CCl_4) 1718 cm^{-1} (ester); nmr (CCl_4) τ 1.8–2.9 (multiplet, 5 H), 4.8–5.3 (multiplet, 1 H), 5.8–6.3 (multiplet, 1 H), 7.5–8.9 (multiplet, 8 H). The multiplet at 4.8–5.3 was assigned to the tertiary hydrogen next to the benzoate group, by analogy with a similar resonance in the nmr spectrum of cyclohexyl benzoate. No parent ion was found in the mass spectrum: m^+/e 202 $(M - HCl)^+$, 123 $(PhCO_2H_2)^+$, 105 $(PhCO)^+$, 81 $(C_6H_9)^+$.

Reaction of Chlorine with Sodium Benzoate and Cyclohexene. A 0.44 *M* solution of chlorine in carbon tetrachloride (40 ml) was added dropwise to a well-stirred mixture of sodium benzoate (10 g, 70 mmoles) in cyclohexene. The reaction mixture was filtered and the solid (9.7 g) was shown to contain no more than 5 mole % chloride ion. The filtrate was extracted with aqueous sodium bicarbonate, dried, evaporated, and analyzed by nmr. The spectrum was consistent with that of dichlorocyclohexane, and did not show the characteristic resonances (τ 1.8–2.9, 4.8–5.3) of 2-chlorocyclohexyl benzoate.

Reaction of Tetraethylammonium Chloride with Benzoyl Peroxide and 2,3-Dimethylbutane. To solutions of tetraethylammonium chloride (0.38 *M*) in acetonitrile (1.0 ml) were added 2,3-dimethylbutane (0.5 ml) and a quantity of benzoyl peroxide in the range 0.09–1.64 mmoles. After heating the sealed, degassed ampoules to 98° for 1.25 hr, bromobenzene was added to each as a glpc standard for analysis (SE30, 80°). Chlorobenzene and the isomeric chlorinated 2,3-dimethylbutanes were produced in the quantities indicated by Figure 2. The actual quantities of each isomer produced in these experiments are given in Table IV.

Table IV. The Reaction of Tetraethylammonium Chloride (0.38 Mmole) with Benzoyl Peroxide and 2,3-Dimethylbutane

Benzoyl peroxide, mmole	1-Chloro-2,3-dimethylbutane, mmole × 10^2	2-Chloro-2,3-dimethylbutane, mmole × 10^2	Selectivity per H
0.10			
0.17	0.35	0.32	5.6
0.18	0.45	0.38	5.1
0.22	0.76	0.71	5.6
0.26	1.36	1.20	5.3
0.30	2.10	1.66	4.7
0.36	3.34	3.02	5.4
0.41	2.17	3.09	8.5
0.48	5.43	6.45	7.1
0.58	6.08	7.31	7.2
0.83	8.47	16.7	11.8
1.21	7.05	14.5	12.3
1.62	6.68	14.5	13.0

Polymerization Studies. A mixture of freshly distilled styrene (60 ml) and dry acetonitrile (60 ml) was divided into four portions, one of which was left to serve as a control. To each of the other three was added benzoyl peroxide (0.25 g) and to two of these three was added tetraethylammonium chloride (0.10 and 1.00 g). The sealed ampoules were heated to 100° for 1 hr and after cooling methanol (100 ml) was added to the solution. The precipitated polystyrene was filtered and weighed. The yield of polymer is shown in Table I.

Chlorination with the Hunsdiecker Intermediate. Duplicate 0.24 *M* solutions of chlorine in acetonitrile (2.0 ml) were allowed to react with dry silver benzoate (200 mg, 0.88 mmole) and filtered through a fritted disk into 2,3-dimethylbutane (0.5 ml). The solutions were degassed and irradiated at 40° for 2 hr with two 200-W tungsten lamps, when the yellow color was discharged. Glpc analysis (SE30, 80°) indicated the formation of 1-chloro-2,3-dimethylbutane (0.28 mmole) and 2-chloro-2,3-dimethylbutane (0.17 mmole).

Reaction of Hydrogen Chloride with Benzoyl Peroxide. To aliquots of a 0.44 *M* solution of hydrogen chloride in dry acetonitrile (1.0 ml) was added a quantity of benzoyl peroxide in the range 0.13–1.62 mmoles. The sealed, degassed ampoules were heated to 98° for 1.5 hr and then analyzed by glpc (SE 30, 90°) using bromobenzene as standard. Since there was too little chlorobenzene present to be isolable (Figure 3), the products were shown to be identical on glpc both with authentic chlorobenzene and with the reaction mixture produced in the reaction of tetraethylammonium chloride above.

Reaction of Hydrogen Chloride with Benzoyl Peroxide and 2,3-Dimethylbutane. To mixtures of 2,3-dimethylbutane (0.5 ml) and a 0.44 *M* solution of hydrogen chloride in dry acetonitrile (1.0 ml) was added benzoyl peroxide in quantities varying between 0.09 and 1.60 mmoles. The sealed, degassed mixtures were heated to 98° for 1.5 hr, and then analyzed by glpc (SE 30, 85°) after adding bromobenzene as a standard. No chlorobenzene could be detected among the products. Only at high concentrations of benzoyl peroxide was any primary alkyl chloride (1-chloro-2,3-dimethylbutane) detected, and even then it always comprised <1% of the total alkyl chloride. The optimum yield of 2-chloro-2,3-dimethylbutane was 90% (Figure 3).

Determination of Selectivities with the Hydrogen Chloride/Peroxide Reagent. To triplicate series of solutions (1.0 ml) of hydrogen chloride (0.32 *M*) in acetonitrile were added benzoyl peroxide and either *n*-butane or isobutane. The reaction mixtures were degassed and heated to 100° for 2.5 hr. Glpc analysis (25 ft Ucon Polar 50HB 2000, 50°) was used to determine primary:secondary and primary:tertiary selectivities. The results of these experiments are to be found in Table II.

Reaction of Deuterium Chloride with Benzoyl Peroxide and 2,3-Dimethylbutane. To duplicate 0.70 *M* solutions of deuterium

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[31] S. D. Andrews and J. C. Smith, *Chem. Ind.* (London), 1376 (1965).

chloride in dry acetonitrile (1.0 ml) was added 2,3-dimethylbutane (0.1 ml). These solutions, which were used as controls, were degassed, sealed, and heated to 98° for 1 hr. Recovery of the hydrocarbon by preparative glpc (Ucon Polar, 70°) showed that no incorporation of deuterium had taken place. Two similar solutions were prepared, but to each of these was added benzoyl peroxide (0.70 mmole). They were degassed, sealed, and heated to 98° for 1 hr. The results of analyses for both deuterium incorporated into the unreacted hydrocarbon (mass spectrometry) and for alkyl chloride produced (glpc, SE30, 85°) are to be found in Table III.

Reaction of Deuterium Chloride with Benzoyl Peroxide and Cyclohexane. To duplicate 0.60 *M* solutions of deuterium chloride in dry acetonitrile (1.0 ml) were added cyclohexane (0.1 ml) and benzoyl peroxide (0.58 mmole). The sealed, degassed ampoules were heated to 98° for 1 hr. Analysis for deuterium incorporation into the unreacted cyclohexane, and for formation of cyclohexyl chloride, gave the results shown in Table III. Control experiments in which the benzoyl peroxide was omitted gave no incorporation of deuterium.

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Structures in Solution of the Yellow and White Forms of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate[1]

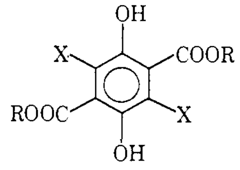
David Y. Curtin and Stephen R. Byrn[2]

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received February 17, 1969*

Abstract: The puzzling dependence of the color (and spectra) of solutions of dimethyl 2,5-dihydroxy-3,6-dichloroterephthalate (I) on the nature of the solvent has now been found to be due to the presence of three species in a solvent-dependent equilibrium. One (Y-I) has intramolecular hydrogen bonds to the carbonyl oxygen atoms at each end of the molecule; the second (W-I) has two intramolecular hydrogen bonds to the chlorine atoms; and the third (H-I) is a hybrid with one hydrogen bond to a carbonyl group and the other to a chlorine atom. Application of a statistical treatment of the uv spectra of solutions in cyclohexane, carbon tetrachloride, chloroform, and mixtures of these with ethanol gives ratios of these three species which are in agreement with results from infrared studies. Replacement of the hydroxyl protons by deuterons is shown to shift the hydrogen-bonded carbonyl stretching vibration (in chloroform solution) to lower frequency but not the unbonded carbonyl vibration.

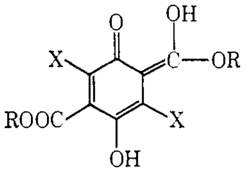
Dimethyl sulfoxide has been found to be unusually effective at breaking up hydrogen bonds to the carbonyl oxygen atoms, and the same behavior is observed when it is employed as a solvent for ir spectra of other hydroxy esters such as methyl salicylate.

In the years between 1882 and 1915, studies[3] of 2,5-dihydroxyterephthalic acid, its 3,6-dihalo derivatives, and their esters A showed that they frequently could be isolated in a yellow or green and a white modification and gave solutions whose uv-visible spectra depended on the nature of the solvent. The structural basis of these observations was a matter of considerable controversy; it was proposed by Hantzsch[3b] that the colored species were enols with the structure B and the white species the dihydroxy diesters A. It was striking that the half-substituted halo acid and its esters C have shown no evidence of the existence of such binate members. In a previous communication[4] we have reported that the two crystalline forms of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (I) were each true dihydroxy diesters but differed in the nature of their hydrogen bonding, the yellow isomer having strongly hydrogen-bonded carbonyl groups and the white having hydrogen-bonded chlorine atoms. We now present evidence that primary species present in dilute carbon tetrachloride or chloroform solutions of I are the yellow substance Y-I with intramolecular hydrogen bonds to the carbonyl oxygen atoms, the colorless substance (W-I) with the intramolecular hydrogen bonds directed to the chlorine atoms, and the hybrid compound H-I.

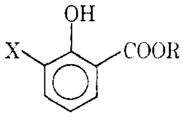


A

I, R = CH_3; X = Cl



B



C

A 2% solution in chloroform of either crystalline solid Y-I or W-I shows two well-defined absorption maxima in the carbonyl stretching region at 1742 and at 1679 cm^{-1} corresponding to the absorptions at 1700 cm^{-1} in the spectrum of the white crystalline form and 1666 cm^{-1} in that of the yellow solid. As was observed with the spectra of the solids[4] exchange of the hydroxylic protons for deuterium shifted the lower frequency absorption in chloroform solution from 1679 to 1666 cm^{-1}

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(2) Sinclair Oil Co. Fellow, 1966–1967. National Science Foundation Fellow, 1967–1968.

(3) See (a) A. Hantzsch, *Chem. Ber.*, 48, 797 (1915); (b) *ibid.*, 48, 785 (1915).

(4) D. Y. Curtin and S. R. Byrn, *J. Am. Chem. Soc.*, 91, 1865 (1969).