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Reactions of Peroxides with Halide Salts. Electrophilic and Homolytic Halogenations

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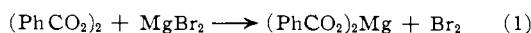
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The halogenation of aromatic substrates is accomplished with a homogeneous solution of benzoyl peroxide and lithium halide in acetic acid or acetonitrile. Lithium bromide reacts almost instantaneously with benzoyl peroxide and anisole to form bromoanisoles in quantitative yields, and at 65° lithium chloride forms chloroanisoles in similar high yields. The yields of halogenated products fall off with the reactivity of the aromatic component in a manner typical of electrophilic substitutions (anisole, 90–100%; toluene, 82–95%; benzene, 45–60%; chlorobenzene, 20–30%; nitrobenzene, nil). In most cases benzoic acid can be isolated in quantitative yields (2 moles per mole of peroxide). The isomer distributions of the halogenated products are the same as those obtained from molecular halogen: anisole (Cl), 24% *ortho*, 76% *para*; (Br), 4% *ortho*, 96% *para*; toluene (Cl), 61% *ortho*, 39% *para*; chlorobenzene (Cl), 30% *ortho*, 70% *para*. The reaction of benzoyl peroxide and lithium chloride in the presence of less reactive aromatics such as benzene and nitrobenzene also produces minor amounts of side products such as carbon dioxide (1–4%), methyl chloride (~1%), benzene (<0.5%), chlorobenzene (1–2%), biphenyl (<0.5%), and chlorine. The decomposition of peroxides is markedly accelerated by halide ion. Thermolysis of benzoyl peroxide in 50% acetic acid–toluene proceeds with a half-life of approximately 20 hr. at 65° and does not contribute significantly to the halide reaction, which is half over in less than an hour. The reaction is first order in benzoyl peroxide and first order in lithium chloride. The reaction with anisole is too rapid to follow at these temperatures. The rate of peroxide disappearance with chloride ion in acetic acid–toluene solutions is independent of cupric or ferric ion and only slightly affected by air. However, the products of the reaction are highly dependent on these additives. Significantly, in the absence of air, benzyl chloride (84–95%) is the major product and chlorotoluenes are only formed in minor amounts (2–6%). This reaction is unaffected by light. In strong contrast, the reaction in air or cupric chloride (catalytic amounts) forms very little benzyl chloride (3–8%) and chlorotoluenes (82–95%) are the major products. Reactions conducted in limited amounts of air give mixtures of benzyl chloride and chlorotoluenes in proportion to the oxygen content. Together these products account for 85–95% of the material balance. Small amounts of benzaldehyde (4–6%) accompany the chlorotoluenes in air but not in the presence of cupric chloride. The roles which benzoyl hypochlorite and molecular chlorine play in these electrophilic and homolytic halogenations are discussed.

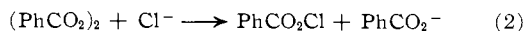
Introduction

Nucleophilic displacements on oxygen are relatively rare except in cases like peroxides where reaction with such nucleophiles as amines, sulfides, sulfoxides, and phosphines have been reported.¹ The study of halides as nucleophiles has been largely restricted to aqueous solutions of monosubstituted peroxides, although the reaction with iodide forms the basis for the analysis of a variety of organic peroxides.² The mechanism of the latter reactions is not established nor are the reactions of peroxides with other halides generally recognized.

In connection with a study of peroxides and Grignard reagents, Lawesson and Yang³ showed that benzoyl peroxide reacts with magnesium bromide in an etheral solution of cyclohexene to produce 1, 2-dibromocyclohexane. They postulated the reaction to proceed *via* molecular bromine.



Bamford and White⁴ studied the decomposition of benzoyl peroxide by lithium chloride in N,N-dimethylformamide solution. In the initial stages, the reaction was first order in peroxide and lithium chloride. Study of the products was complicated by the lability of DMF, but was accounted for by assuming the formation of molecular chlorine and benzoyl hypochlorite. They postulated the primary process to be a nucleophilic displacement by chloride ion



In the course of our studies of the decomposition of

peroxides by catalytic amounts of transition metal salts⁵ we found that benzoyl peroxide reacted with halide salts in the presence of aromatic substrates to produce aryl halides. In this report we wish to present studies of electrophilic and homolytic halogenations employing this system.

Results

Lithium Chloride.—The rate of decomposition of benzoyl peroxide is markedly affected by the presence of halide ion. For example, in 50% v. benzene–acetic acid solution at 65°, benzoyl peroxide (0.05 M) is less than 1% decomposed in 80 min. Under the same conditions but with 0.1 M lithium chloride, the peroxide is 50% decomposed as shown in Fig. 1. When carried to completion, the latter reaction yielded typically: 0.11 mole of chlorobenzene, 1.78 moles of benzoic acid, 0.14 mole of carbon dioxide, 0.02 mole of methyl chloride, 0.015 mole of chlorine, and a small amount of biphenyl, for each mole of benzoyl peroxide decomposed. No phenyl benzoate or acetate was detected. A transient intermediate whose maximum concentration was attained at approximately 40 min. was detected by examining the infrared spectrum at 757 cm.⁻¹ (*t*-butyl hypochlorite 760 cm.⁻¹) of the crude reaction mixture. The possibility that it was benzoyl hypochlorite as described by Bamford and White⁴ could not be established.

Nuclear Halogenation of Aromatic Compounds.—The decomposition of benzoyl peroxide in the presence of lithium chloride ions was also studied in acetic acid solutions of other aromatic compounds. A small amount of cupric chloride was added to inhibit free-radical chain processes (*vide infra*). In benzene–acetic acid solutions its presence did not affect the rate of peroxide decomposition, although the yield of chlorobenzene was increased and that of carbon dioxide de-

(1) For an enlightening review see J. O. Edwards, "Peroxides Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 5.

(2) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 333f.

(3) S. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 4230 (1959).

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

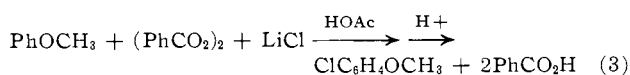
(5) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).

TABLE I
 HALOGENATION OF AROMATIC COMPOUNDS WITH BENZOYL PEROXIDE AND LITHIUM HALIDE^a

Aromatic compound	Reactants			Reaction time, hr.	Gas, ^b ml.	Products			Isomer distribution, %	
	(PhCO ₂) ₂ , mole	LiCl, mole	CuCl ₂ , mole			PhCO ₂ H, mole (%) ^c	ArCl		<i>ortho</i>	<i>para</i>
Chlorobenzene	0.10	0.15	0.10	18	95 ^d	0.09 (45)	Dichlorobenzene 0.23	23	30	70 ^h
Nitrobenzene	.0080	.035	.0080	23	27 ^e	.005 (31)	None ^f	0
Toluene	.10	.15	.10	18	25	.16 (80)	Chlorotoluenes .084 ^g	84	61	39
Toluene ⁱ	.10	.15	.10	66	50	.175 (88)	Chlorotoluenes .087 ^g	87	61	39
Toluene	.10	.20	.010	30	30	.185 (93)	Chlorotoluenes .092 ^g	92	61.5	38.5
Toluene	.050	.10	.0050	24	Trace	.092 (92)	Chlorotoluenes .045	90	61	39
Toluene	.050	.10	.0025	24	Trace	.085 (85)	Chlorotoluenes .047	94	61	39
Toluene	.050	.20	0	26	Nil	.093 (93)	Chlorotoluenes .0050	10	60	40
Toluene	.0080	.020	0	50	Nil	.015 (94)	Benzyl chloride .0046	92
Toluene	.0080	.020	0	50	Nil	.015 (94)	Chlorotoluene .0002	2	~60	~40
Toluene	.0080	.020	0	50	Nil	.015 (94)	Benzyl chloride .0076	95
Anisole	.0500	.20	.0050	24	Trace	.10 (100)	Chloroanisole .049	98	23.5	76.5
Anisole	.025	.10	.0025	6	Nil	.05 (100)	Chloroanisole .025	100	24	76
Anisole	.050	.10	0	24	Nil	.098 (98)	Chloroanisoles .048	96	24	76
Anisole	.050	.10 ^j	0	3	Nil	.097 (97)	Bromoanisoles .049	98	3.5	96.5
Anisole ^k	.050	.10 ^j	0	3	Nil	.097 (97)	Bromoanisoles .048	98	3.5	96.5
<i>tert</i> -Butylbenzene	.050	.10	.0050	22	6	0.100 ^k (100)	Bromoanisoles .078	96	4	96
Benzene	.050	.10	.0050	22	25	.088 (88)	Chlorobutylbenzene	78	19	81
Benzene	.050	.10	.0050	22	25	.061 (61)	Chlorobenzene ^l .027	38
Benzene	.050	.10	0	24	130	.083 (83)	Chlorobenzene	54

^a In 50% v. aromatic compound in glacial acetic acid at 65°. ^b Mostly carbon dioxide, minimum amounts of methyl chloride. ^c Yields based on 2 moles of benzoic acid per mole peroxide. ^d Contains methyl chloride (~10 ml.) and chlorine. ^e Contains 12 ml. of methyl chloride. ^f Chlorobenzene (0.001 mole), benzene (0.0004 mole), and chlorine. ^g Traces of benzyl chloride, chlorobenzene. ^h *meta* and *para* isomers, mixture mostly *para* by infrared analysis. ⁱ Acetonitrile solvent. ^j Lithium bromide. ^k Titration yields 0.48 mole of benzoic acid, 0.052 mole of lithium benzoate. ^l In addition to benzene and biphenyl.

creased. The extent to which the aromatic constituent was chlorinated depended on the nature of the ring substituent, as shown in Table I. In general, good yields of aryl halides were obtained with aromatic compounds which are reactive to electrophilic substitution.⁶ The high yields of benzoic acid parallel the reactivity of the aromatic substrate, and in general less carbon dioxide, methyl chloride, and other side products were evident in these cases. For example, the reaction with anisole followed the stoichiometry given in eq. 3 almost quantitatively. No carbon dioxide was liberated.



As shown in Fig. 2, the rate of disappearance of peroxide (measured spectroscopically by infrared absorption) also followed the reactivity of the aromatic compound, being fastest in anisole and slowest in nitro-

benzene. In these runs the aromatic substrate also partially served as solvent.

The relative reactivity of aromatic compounds was examined quantitatively by conducting competitive chlorination in solutions containing mixtures of benzene and toluene in the presence of catalytic amounts of cupric chloride to inhibit side chain halogenation. At molar ratios of benzene to toluene of 30 and 80 the relative molar reactivity of benzene to toluene was 0.0030 and 0.0035.

The formation of chlorine was evident only with the less reactive aromatics, benzene, chlorobenzene, and nitrobenzene. Quantitative estimation was difficult, but color of the solution, odor, and decolorization of starch-iodide paper held above the mixture indicated its presence. Titration with iodide-thiosulfate gave a titer which varied from 0.10 to 0.20 mole and probably included the hypochlorite which was not separately determined. When chlorine was detected, the yield of aryl halide was generally low and methyl chloride high. In addition, products from the phenyl moiety derived

(6) P. B. D. DeLaMare and J. H. Ridd, "Aromatic Substitution," Butterworths, London, 1959, p. 131f.

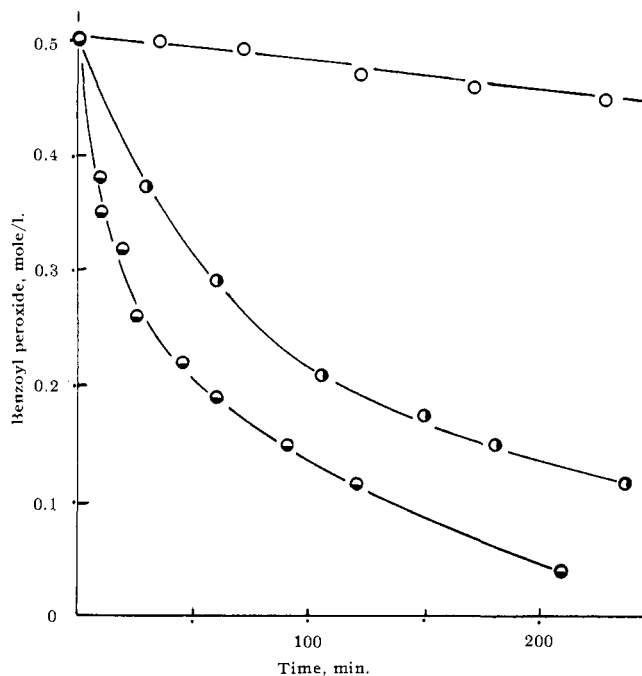
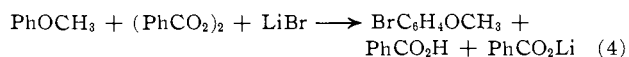


Fig. 1.—Decomposition of benzoyl peroxide in benzene-acetic acid solutions at 65°: ○, no added chloride; ◐, 0.8 *M* lithium chloride; ●, 2 *M* lithium chloride.

from the peroxide were found as benzene, chlorobenzene, and biphenyl in small and varying amounts.

Lithium Bromide.—The reaction of benzoyl peroxide in anisole solutions of acetic acid with lithium bromide at 65° was too rapid to measure conveniently. A transient yellow color developed instantaneously and faded to yield a colorless solution from which 2 moles of benzoic acid and 1 mole of bromoanisoles could be isolated. The complete stoichiometry could be easily obtained in acetonitrile solutions uncomplicated by the presence of a protic solvent. Lithium benzoate precipitated from the reaction mixture, and the mixture could be titrated with acid and base electrometrically.



Unlike the reaction in acetic acid, the brown color of bromine formed instantly, persisted even after 3 hr. at 65° in the less polar acetonitrile solutions. For each mole of peroxide 1 mole of benzoic acid and 1 mole of lithium benzoate were formed. Bromoanisoles were analyzed in 96% yield. The stoichiometry of the reaction is that given in eq. 4. In the absence of benzoyl peroxide, lithium bromide was not oxidized to bromine under these conditions.

Toluene.—The reaction of benzoyl peroxide and lithium chloride in toluene-acetic acid solutions yields two types of products, benzyl chloride and *o*- and *p*-chlorotoluenes, depending on reaction conditions. The reaction conducted in a sealed evacuated vessel from which oxygen had been purged gave principally benzyl chloride (95–99%) and the chlorotoluene mixture was found only in minor amounts (2–3%). This reaction was unaffected by light. In strong contrast, the reaction in air (lightly closed vessel) gave very little benzyl chloride (3–8%), and chlorotoluenes (79–93%) were the major products together with small amounts (4–6%) of benzaldehyde.

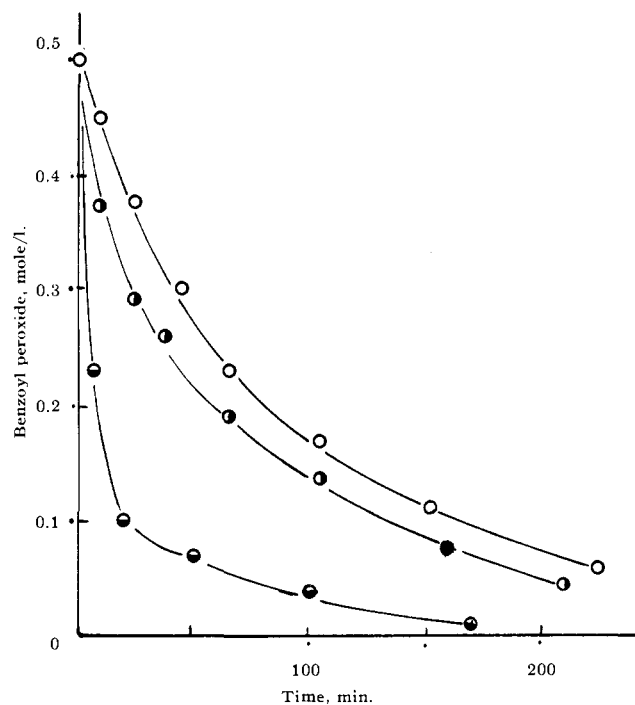


Fig. 2.—Decomposition of benzoyl peroxide in 1 *M* lithium chloride solutions of aromatic compound and acetic acid at 65°: ○, benzene; ◐, toluene; ●, anisole.

Reactions conducted in limited amounts of air gave mixtures of benzyl chloride and chlorotoluenes in proportion to the oxygen content. Together these products accounted for 85–95% of the material balance. Chlorotoluenes were also the major products (90–95%) when benzoyl peroxide and lithium chloride react in the absence of air but in the presence of catalytic (1%) amounts of cupric or ferric chloride. Benzyl chloride (2–4%) was a minor product and no benzaldehyde was formed. The phenyl moiety from the peroxide was accounted for mainly as benzoic acid (85–95%) and small amounts of carbon dioxide, methyl chloride, and benzene were found.

In the absence of cupric chloride, the amount of side chain halogenation was a sensitive measure of the oxygen present in the system. On the basis of the yield of benzyl chloride in the presence of varying amounts of oxygen, it can be estimated that the average chain length for the radical chain halogenation is approximately 10^3 .

The kinetics of the peroxide disappearance in toluene-acetic acid solutions was followed by measuring the absorption band at 998 cm^{-1} in the infrared spectrum. In 44% v. toluene in acetic acid at 65°, the reaction was first order in benzoyl peroxide and in lithium chloride in the concentration range 0.05–0.30 *M* peroxide and 0.20–0.9 *M* lithium chloride. Since the aromatic constituent was present in large excess, the dependence of the rate on its concentration was not determined quantitatively. The pseudo-second-order rate constant in 44% v. toluene-acetic acid was $9.8 \times 10^{-5} \text{ l./mole-sec.}$ and fell off as the peroxide decomposition exceeded 50–60% as found by Bamford and White.⁴ In the first 10–15% of the reaction, the rate in air was the same as that in an evacuated system but fell off slightly faster as the reaction proceeded (e.g., after 4 hr. the former was 66% complete and the latter 55% complete). Extensive kinetic studies were not con-

ducted since the results in dimethylformamide have already been published.⁴

Further experiments were conducted at 65° in acetic acid solutions in the absence of air and cupric chloride to determine the nature of the chain-transfer step of the side chain halogenation. Intermolecular competition between toluene and cyclohexane for the chlorinating species from benzoyl peroxide and lithium chloride was compared to molecular chlorine under similar conditions. In each case the relevant products were *o*- and *p*-chlorotoluenes, benzyl chloride, and cyclohexyl chloride. Under the conditions of these experiments benzyl chloride and cyclohexyl chloride are stable and such complicating side reactions as the formation of benzyl acetate, bibenzyl, cyclohexene, and cyclohexyl acetate were not evident. The results of representative examples are shown in Table II.

TABLE II
CHLORINATION OF TOLUENE-CYCLOHEXANE MIXTURES^a

Chlorinating agent (<i>M</i>)	Solvent ^b (<i>M</i>)	ClC ₆ H ₄ -CH ₃ , ^c %	C ₆ H ₅ -CH ₂ Cl, %	C ₆ H ₁₁ Cl, %	<i>k</i> _α / <i>k</i> _{CY} ^d
Cl ₂ (0.17)	T (6.31)	0	13.7	67.3	0.40
	CY (3.01)				
Cl ₂ (.19)	T (4.01)	0	6.96	77.0	.49
	CY (5.41)				
Cl ₂ (.30)	T (8.0)	0	36.0	49.1	.51
	CY (1.4)				
Cl ₂ (.051)	T (1.0) HOAc	7.4	17.4	68.5	.45
	CY (0.50)				
Cl ₂ (.051)	T (1.0) HOAc	2.0	41.6	56.4	.58
	CY (0.20)				
B.P. ^e (.10)	T (3.6) HOAc	8.1	55.2	36.7	1.6
LiCl (.10)	CY (1.1)				
B.P. (.10)	T (3.6) HOAc	7.5	45.0	47.5	1.1
LiCl (.20)	CY (1.1)				
B.P. (.10)	T (3.6) HOAc	18.9	42.4	39.4	1.2
LiCl (.30)	CY (1.1)				
B.P. (.10)	T (3.6) HOAc	18.0	34.5	47.5	0.85
LiCl (.40)	CY (1.1)				

^a At 50.2° and irradiated with a 100-watt Mazda lamp.
^b T = toluene, CY = cyclohexane. ^c Composition of mixture; 62% *ortho*, 38% *para*. ^d Per reactive C-H bond. ^e B.P. = benzoyl peroxide.

The relative reactivity ratio of toluene and cyclohexane is essentially the same in a largely hydrocarbon solvent as it is in acetic acid solutions, and it varies only slightly between 0.40 and 0.50 over a range of mole ratios of reactant hydrocarbons. The same relative reactivity under equivalent conditions of solvent and temperature is not obtained with benzoyl peroxide and lithium chloride as shown in Table II. This ratio varies with chloride salt concentration and decreases with increasing chloride concentration, and it approaches the value obtained from molecular chlorine.

Experimental

Materials.—Benzoyl peroxide, Lucidol Co., recrystallized from chloroform-methanol solution; lithium chloride, Mallinckrodt AR reagent; lithium bromide, Mallinckrodt AR reagent; acetic acid, du Pont Co., reagent grade; benzene, Eastman Kodak, Spectrograde; toluene, Mallinckrodt AR reagent redistilled through a 15-plate Oldershaw column; *t*-butylbenzene, Phillips Petroleum Co., research grade; chlorobenzene, Eastman White Label; nitrobenzene, Fisher reagent grade; *p*-xylene, Eastman White Label; styrene, Dow Chemical Co., washed with sodium hydroxide, dried, and distilled *in vacuo*; acetonitrile, Matheson Co., redistilled from phosphorus pentoxide; cyclohexane, Eastman White Label.

Benzoyl Peroxide and Lithium Chloride. Typical Procedure.—Benzoyl peroxide (121 g., 0.05 mole) and lithium chloride (4.1 g., 0.10 mole) were dissolved in a solution of 50 ml. of aromatic compound and 50 ml. of acetic acid in a two-necked 300-ml. round-bottomed flask equipped with a magnetic stirrer. A gas

outlet was led into an inverted buret filled with water to measure gas evolution. The solution was swept with oxygen-free nitrogen *via* a three-way stopcock connected to the gas burets, and heated with stirring at 65° for approximately 24 hr.

The mixture was shaken with excess water (500 ml.) and the organic phase re-extracted twice with aqueous sodium carbonate solution. Benzoic acid was recovered from the aqueous solutions, dried, and weighed. The organic phase after drying with calcium chloride was fractionated to obtain the aromatic halide. The infrared spectrum of the aromatic halide was compared with an authentic or mixtures of authentic isomeric samples in order to check the identity and composition. The organic phase was also analyzed quantitatively by gas-liquid chromatography using the internal standard method; retention times (min.), DEGS (diethylene glycol succinate, 124°): chloroanisoles, *o*- 5.3, *p*- 7.2; bromoanisole, *o*- 9.7, *p*- 12.1; chloroform, 2.3; *o*- 6.5, *m*- and *p*-dichlorobenzene, 7.5; Carbowax (187°): chlorobenzene, 3.0; *p*-dichlorobenzene, 6.3; benzyl chloride, 7.7; chlorotoluenes, 4.2; ODPN (oxydipropionitrile, 86°): chlorobenzene, 5.6; chlorotoluenes, *o*- 10.5, *p*- 12.0; *p*-dichlorobenzene, 18.1; silicone SF 96: chloro-*t*-butylbenzenes, *o*- 15, *m*- and *p*- 18.

The isomer distribution for chlorotoluene was first determined by g.l.c. and then checked quantitatively by infrared (805 cm.⁻¹ band for *p*-chlorotoluene and 746 cm.⁻¹ band for *o*-). The results on Beckman IR-7 checked the g.l.c. results as shown in Table I to within 1%.

Rate Studies.—The rate of disappearance of benzoyl peroxide was followed by measuring the disappearance of the 995 cm.⁻¹ band in the infrared spectrum. A Beer's law plot was used in calculating the peroxide concentration. The reaction mixture as described above was placed in a constant temperature bath (65 ± 0.1°) and a 2-ml. sample was removed from the reaction mixture periodically and quenched by adding it to a known amount of the aromatic solvent and excess water. The sample was shaken, then separated, and shaken again with sodium carbonate solution. The organic layer was then dried over calcium chloride and the infrared spectrum taken in matched 0.1-mm. cells against the aromatic solvent.

Since the metal needle of the hypodermic syringe needle reacted with peroxidic solution of the halide to introduce metal ions into the reaction mixture, samples were extracted with a glass pipet. These reactions studied in the absence of air were conducted in multiple evacuated ampoules which were periodically removed from the constant temperature bath. Kinetic runs made in this manner yielded results which were reproducible to within 3%. The reactions with toluene also gave reproducible kinetic results for peroxide disappearance. However, the distribution between benzyl chloride and the isomeric chlorotoluenes was difficult to obtain because of its extreme sensitivity to oxygen. The *ortho-para* ratio was unaffected within the limited reaction conditions employed.

Determination of Benzoic Acid and Lithium Benzoate Yields by Titration.—Benzoyl peroxide (12.1 g., 0.05 mole) was placed in a flask. To this was added a solution of 8.7 g. of lithium bromide in 75 ml. of acetonitrile and 50 ml. of anisole. An immediate yellow color developed and a precipitate of lithium benzoate filled the flask. After heating at 65° for about 3 hr. the reaction solution was poured into 800 cc. of water. The anisole layer was separated and titrated with 0.1 *N* sodium hydroxide to the phenolphthalein end point (0.0378 mole of benzoic acid present). An aliquot of the water layer was titrated in the same manner and indicated that 0.016 mole of free benzoic acid was dissolved in the aqueous phase, or a total of 0.054 mole of free benzoic acid.

Another aliquot of the water phase was taken and titrated with 0.1 *N* hydrochloric acid to a pH of about 2.9 with a pH meter. The break in the titration curve was the end point for the titration of lithium benzoate to benzoic acid. This result indicated a yield of 0.052 mole of lithium benzoate from the reaction. One mole of free benzoic acid and 1 mole of the benzoate salt are thus produced per mole of peroxide.

Competitive Chlorinations.—Russell's procedure⁷ for free-radical chlorination with molecular chlorine was repeated for our studies in acetic acid. A deaerated solution of toluene and cyclohexane in acetic acid was irradiated with a 100-watt frosted Mazda lamp in a water bath at 50.2° as a slow stream of chlorine entrained in nitrogen was introduced. The reaction mixture was washed with excess water and sodium carbonate solution, dried

(7) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957).

over calcium chloride, and analyzed by g.l.c. on a 6-ft. column packed with 20% SF 96 (General Electric Co. silicone fluid) on Chromosorb W, 60-80 mesh, at 125°. Retention times: cyclohexane, 2.8; toluene, 4.6; chlorobenzene, 6.6; cyclohexyl chloride, 8.5; *o*- and *p*-chlorotoluenes, 11.7; benzyl chloride, 15.4. Cyclohexene, cyclohexyl acetate, and benzyl acetate were not detected. Authentic mixtures of benzyl chloride and chlorotoluenes were made up and shown to be stable under the reaction conditions, and to be analyzed by g.l.c. to within 3% reproducibility. These results are shown in Table II.

The reactions with benzoyl peroxide and lithium chloride were done under similar conditions. A solution of lithium chloride in acetic acid was added to a mixture of cyclohexane and toluene of the desired mole ratio, flushed with nitrogen, sealed *via* a mercury trap, and placed in the thermostated bath for varying lengths of time. Unreacted peroxide was determined by infrared, and did not interfere with the analysis of the chlorotoluene mixture.

Synthesis of β -Chloro- α -phenethyl Acetate.—To a solution of freshly redistilled styrene (20.7 g., 0.2 mole) in 200 ml. of acetic acid was added *t*-butyl hypochlorite (17.2 g., 0.16 mole). The exothermic reaction was moderated by cooling in a water bath, and the yellow color disappeared in approximately 5 min. The mixture was poured into excess water and extracted with ether. The ether solution was washed with water, extracted with sodium bicarbonate solution, dried, and distilled. It yielded 14 g. of the chloroacetate boiling at 88-90° (0.5 mm.), n_D^{30} 1.5074 (lit.⁸ b.p. 101-104° (3 mm.); n_D^{20} 1.5182).

Reaction of Styrene with Benzoyl Peroxide-Lithium Chloride.—A solution containing benzoyl peroxide (12.1 g., 0.05 mole), lithium chloride (4.1 g., 0.10 mole), and styrene (10.4 g., 0.1 mole) in 100 ml. of glacial acetic acid was warmed at 65° for 8 hr. The mixture was poured into water and extracted with chloroform. The chloroform extract was washed with sodium bicarbonate twice, dried on calcium chloride, and distilled. It yielded 13 g. of a mixture of products whose infrared spectrum indicated acetates and benzoates. The reaction was complicated by the formation of polystyrene.

If the same reaction was carried out in the presence of small amounts of cupric chloride (0.4 g., 0.003 mole) no polystyrene was formed.⁹ Benzoic acid (5.9 g.) and a mixture of adducts (11.4 g.) containing mainly benzoate esters were formed. Little or no β -chloro- α -phenethyl acetate was formed.

Discussion

The first-order thermal (80-90°) decomposition of benzoyl peroxide in acetic acid solution leads to a spectrum of products characteristic of a benzoyloxy radical as an intermediate,¹⁰ among which are benzene, biphenyl, phenyl benzoate, benzoic acid, *p*-phenylbenzoic acid, homophthalic acid, homoterephthalic acid, and carbon dioxide. Benzoic acid is a minor product. The thermal decomposition of benzoyl peroxide in the presence of lithium chloride is pseudo-second order (first order in benzoyl peroxide and lithium chloride). The dependence of the rate on the aromatic constituent employed in large excess as solvent was not determined quantitatively. The aromatic hydrocarbon is not required in the reaction of benzoyl peroxide and lithium chloride since Bamford and White⁴ have reported on the kinetics in *N,N*-dimethylformamide alone. The reaction of benzoyl peroxide and lithium chloride in solutions of aromatic compounds and acetic acid proceeds readily at lower temperatures (50-65°) than required for the purely thermal decomposition and it generates almost 2 moles of benzoic acid per mole of peroxide even in the absence of a substrate capable of being halogenated. Two moles of benzoic acid are obtained in the presence of reactive

aromatic compounds such as anisole and no carbon dioxide is liberated. The reaction is much faster with lithium bromide than chloride and produces a mole of bromine which can be determined quantitatively in acetic acid or acetonitrile solutions. For example, under equivalent conditions when the reaction with lithium chloride is half complete at 150 min. at 65° in anisole the reaction with lithium bromide is half complete in a few minutes. The stoichiometry of both reactions is the same.

In the presence of an aromatic constituent the rate of disappearance of peroxide is related to the reactivity of the aromatic compound to electrophilic attack. Thus, the reaction in anisole or styrene is faster than it is in benzene or nitrobenzene. The high yields of chlorinated products and faster rates in the presence of these reactive substrates are in line with an electrophilic substitution. The isomeric composition of the chlorinated aromatics and their relative reactivities to chlorination indicate that the species involved in the nuclear substitution is molecular chlorine.

In Table III the isomer distribution obtained in the

TABLE III
ISOMER DISTRIBUTION IN THE CHLORINATION OF AROMATIC COMPOUNDS

Aromatic compound	Chlorinating agent	— Aryl chlorides —			Reference
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
C ₆ H ₅ CH ₃	(PhCO ₂) ₂ -LiCl	62	..	38	This study
C ₆ H ₅ CH ₃	Cl ₂ -HOAc	59.7	0.5	39.8	11
C ₆ H ₅ CH ₃	Cl ⁺ -HOAc ^a	74.6	2.2	23.2	12
C ₆ H ₅ CH ₃	ClOAc-HOAc	72.2	..	27.9	13
C ₆ H ₅ C(CH ₃) ₂	(PhCO ₂) ₂ -LiCl	19	..	81	This study
C ₆ H ₅ C(CH ₃) ₂	Cl ₂ -HOAc	21.5	2.29	76.2	14
C ₆ H ₅ C(CH ₃) ₂	Cl ⁺ -HOAc-H ₂ O	(58)	..	42	12
C ₆ H ₅ OCH ₃	(PhCO ₂) ₂ -LiCl	24	..	76	This study
C ₆ H ₅ OCH ₃	Cl ₂ -HOAc	21	..	79	15
C ₆ H ₅ OCH ₃	(PhCO ₂) ₂ -LiBr	4 ^b	..	96 ^b	This study
C ₆ H ₅ OCH ₃	Br ₂ -HOAc	1.6	..	98.4	16
C ₆ H ₅ Cl	(PhCO ₂) ₂ + LiCl	30	..	70 ^c	This study
C ₆ H ₅ Cl	Cl ₂	39	6	55	17

^a Positive chlorine described by DeLaMare, *et al.* (ref. 12).
^b Bromides. ^c Includes *meta* and *para* (not separated), mostly *para* by infrared analysis.

chlorination of several aromatic compounds in this study is compared to those obtained from other chlorinating agents in acetic acid: molecular chlorine, acetyl hypochlorite, and positive chlorine (ClOAcH⁺, ClOH⁺, or Cl⁺).

The relative molecular reactivity of toluene compared to benzene in acetic acid determined by intermolecular competition reactions was in the range 29(0-330) depending slightly on the mole ratio of the reactant hydrocarbons. This compares with a value of 359 for molecular chlorine in acetic acid found by Stock and Brown,¹¹ 145 for acetyl hypochlorite in acetic acid by DeLaMare, Hilton, and Varma¹³ and 56 for positive chlorine (hypochlorous acid in aqueous perchloric acid).¹² In the presence of air or metal halides such as cupric or ferric chloride the nuclear halogenation is the predominant reaction, and the free-radical chain reaction is inhibited.

(11) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5775 (1957).

(12) P. B. D. DeLaMare, J. T. Harvey, M. Hassan, and S. Varma, *J. Chem. Soc.*, 2756 (1958).

(13) P. B. D. DeLaMare, I. C. Hilton, and S. Varma, *ibid.*, 4044 (1960).

(14) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **80**, 5615 (1959).

(15) B. J. Jones and E. N. Richardson, *J. Chem. Soc.*, 3939 (1956); P. B. D. DeLaMare and C. A. Vernon, *ibid.*, 1764 (1951).

(16) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **82**, 1942 (1960).

(17) A. F. Holleman, *Chem. Rev.*, **1**, 187 (1924).

(8) W. E. Rydon and H. N. Hanby, *J. Chem. Soc.*, 114 (1946).

(9) J. K. Kochi, *J. Am. Chem. Soc.*, **79**, 2942 (1957).

(10) M. T. Gladstone, *ibid.*, **76**, 1581 (1954); H. Gilsen and P. H. Hermans, *Ber.*, **58**, 770 (1925); C. G. Swain and A. J. Kresge, *J. Am. Chem. Soc.*, **80**, 5313 (1958); M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Org. Chem.*, **10**, 386 (1945).

However, the free-radical chain chlorination of toluene in the absence of inhibitors is more rapid¹⁸ than the electrophilic substitution in the nucleus even in acetic acid (*vide supra*).¹⁹ The species responsible for the free-radical chlorination in this system was examined by carrying out competition studies with toluene and cyclohexane. The relative reactivities of these compounds to molecular chlorine has been determined by Russell²⁰ and to *t*-butyl hypochlorite by Walling and Jacknow.²¹ We re-examined the relative reactivities in solutions of toluene and cyclohexane in acetic acid under our reaction conditions. As shown in Table IV,

TABLE IV
COMPETITIVE CHLORINATIONS OF TOLUENE AND CYCLOHEXANE WITH CHLORINE

Chlorinating agent	Solvent	Temp., °C.	k_a/k_{CY}^a	Reference
Cl ₂	PhCH ₃ -C ₆ H ₁₂	40	0.35-0.40	22
Cl ₂	PhNO ₂	40	.35- .48	22
Cl ₂	PhCH ₃ -C ₆ H ₁₂	50	.40- .51	This study
Cl ₂	HOAc	50	.50- .54 ^b	This study
Cl ₂	CH ₃ CN	65	.49- .51	This study
(CH ₃) ₂ COCl	PhCH ₃ -C ₆ H ₁₂	40	0.67	21

^a Reactivity of toluene compared to cyclohexane per C-H bond. ^b Value extrapolated from Russell's result is 0.49.

the relative reactivity of toluene to cyclohexane, expressed as k_a/k_{CY} ,²² in acetic acid solution is in the same range as it is in the absence of any extraneous solvent. Aside from a minor solvent effect,^{7,20} these values compare favorably with those obtained earlier by Russell²² and Walling.^{21a} Since high reproducibility was difficult to obtain, especially in the peroxide reactions, a range of reactivity values is given. The relative reactivity of toluene and cyclohexane toward the halogenating species present in the system consisting of benzoyl peroxide and lithium chloride is markedly dependent on the halide salt concentration (or molar ratio of halide salt to peroxide) as shown in Table V.

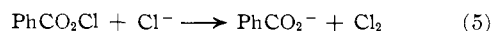
TABLE V
COMPETITIVE CHLORINATION OF TOLUENE AND CYCLOHEXANE WITH BENZOYL PEROXIDE-LITHIUM CHLORIDE^a

Lithium chloride, M	Ratio ^b (Cl ⁻)/(PhCO ₂) ₂	k_a/k_{CY}^c	Radical ^d reaction, %
0.067	0.87	1.59	94
.13	1.74	1.42	92
.20	2.60	1.24	90
.27	3.47	0.86	85
.33	4.33	.65	76
.48	6.62	.48	55
.55	7.93	.47	29

^a In acetic acid solutions of toluene (2.42 M) and cyclohexane (0.71 M) at 50°, benzoyl peroxide (0.077 M). ^b Molar ratio of lithium chloride to benzoyl peroxide. ^c Relative reactivity²² of toluene to cyclohexane per C-H bond. ^d Relative to nuclear substitution; benzyl chloride *vs.* *o*- and *p*-chlorotoluene.

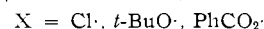
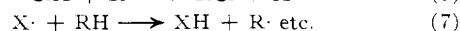
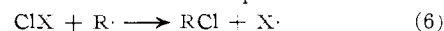
At relatively low halide concentrations, the chlorinating agent(s) is more selective than either molecular chlorine or *t*-butyl hypochlorite but is less selective than bromine²³ ($k_a/k_{CY} = 250$). This selectivity decreases monotonically with increasing halide salt concentra-

tion and approaches the selectivity of these reagents at 0.4 M lithium chloride. At concentrations of lithium chloride greater than approximately 0.45 M, the relative reactivity k_a/k_{CY} is independent of the chloride concentration as shown in Fig. 3. Since these reactions are singularly free of side reactions, we do not believe that this change in selectivity is attributed to adventitious loss or destruction of products. The reaction is also relatively unaffected by the addition of lithium perchlorate and a general salt effect is unlikely. We postulate that the change in selectivity is attributed to a change in concentration of the chlorinating species present in the system with changing chloride salt concentration by a reaction such as (5)²⁴



If reaction 5 is not too rapid, the effect of changing the chloride ion concentration would be to convert benzoyl hypochlorite to molecular chlorine, such that at low chloride concentrations the hypochlorite would be the species mainly responsible for the chlorination and at high chloride concentration it would be chlorine. Since these free-radical chlorinations have long kinetic chain lengths (*infra supra*) such a formulation²⁵ is not unreasonable. Reactions such as (5) are also known with *t*-butyl hypochlorite^{26a} and evidence for its reversibility has been given.⁴ It is interesting to note that the degree to which the free-radical chain process (benzyl chloride formation) competes with electrophilic chlorination also depends on the lithium chloride concentration (Table V). High chloride concentrations where we believe the predominant species is molecular chlorine also favor electrophilic substitution, which is nominal at low chloride concentrations. There is no doubt⁶ that molecular chlorine in acetic acid is an active electrophile.²⁷

These results are not sufficient to allow us to ascertain the degree to which benzoyl hypochlorite and chlorine participate in the radical chain chlorination at any given chloride salt concentration. Even at low chloride concentrations it is possible that appreciable amounts of chlorine are present, although the curve in Fig. 3 extrapolates at zero lithium chloride concentration to a value of k_a/k_{CY} of approximately 1.7. We are presently carrying out independent studies on the properties of benzoyl hypochlorites as a chlorinating agent. The trend toward more selective behavior of benzoyl hypochlorite relative to *t*-butyl hypochlorite and chlorine would not be completely unexpected if one were to compare the reactivities of benzoyloxy^{26b} radical, *t*-butoxy^{21b} radical, and chlorine atom as chain-transfer agents in the radical chain process



(24) Bamford and White⁴ have indicated that reaction 5 is reversible; We have not been able to corroborate their results.

(25) An alternative explanation involving the formation of the trichloride ion, Cl₃⁻, is unlikely in view of the small effect added chloride salts have on chlorinations in acetic acid.

(26) (a) Though expectedly less facile: *cf.* M. Anbar and D. Ginsberg, *Chem. Rev.*, **54**, 965 (1954); M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1094, 1105 (1954); (b) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1572 (1962).

(27) Under slightly different conditions, DeLaMare, *et al.*¹³ indicate that acetyl hypochlorite is more reactive than chlorine. This result is incompatible with the aforementioned statement if acetyl hypochlorite and chlorine are considered to coexist in solution (*vide supra*) unless one allows for equilibration of the benzoyl hypochlorite (reaction 5) under conditions where the slower electrophilic chlorination prevails.

(18) *Cf.* DeLaMare, *ref.* 6, p. 105.

(19) Molecular chlorine in acetic acid in the absence of light or peroxide yields predominantly *o*- and *p*-chlorotoluenes.

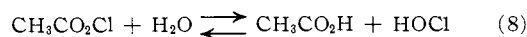
(20) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987, 4997, 5002 (1958).

(21) (a) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108, 6113 (1960); (b) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(22) G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85**, 2976 (1963).

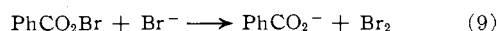
(23) P. C. Anson, P. S. Fredericks, and J. M. Tedder, *J. Chem. Soc.*, 918 (1959).

The value of k_a/k_{CY} is increased slightly by water. For example, if water is deliberately added (3.5 M, ~ 7 wt. %) to the mixture which yields $k_a/k_{CY} = 0.85$ (see Table IV), this ratio is increased to 1.42, and similarly at lower chloride concentrations this ratio is raised from 1.59 to 2.07. DeLaMare, *et al.*,²⁸ have studied the hydrolysis equilibrium 8 and estimated the



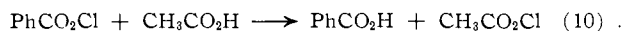
equilibrium constant to be 4×10^4 . Under their conditions, in an acetic acid solution containing 1% water, the predominant species is HOCl. If a similar situation applies to benzoyl hypochlorite in the presence of chloride ion, the increase in k_a/k_{CY} in the presence of water may be attributed to hypochlorous acid.²⁹

A similar reaction of lithium bromide with benzoyl peroxide presumably proceeds through the analogous benzoyl hypobromite intermediate. In this case the rapid development of bromine indicates that such an intermediate is unstable in the presence of bromide and the reaction 9 is very rapid. There is no indication



that such a reaction is reversible to any appreciable extent. Similarly, hypoiodites, though intermediates in the reaction of iodide with peroxides, undoubtedly yield iodine by a rapid reaction with iodide.

The formation of methyl chloride in the presence of unreactive substrates is further evidence that acyl hypohalites are intermediates in these reactions. No evidence for methyl chloride formation could be obtained from the presence of molecular chlorine alone in acetic acid under our reaction conditions. Under circumstances where the concentration of benzoyl hypochlorite is allowed to build up, transchlorination (10) with acetic acid (or acetate ion) can occur.



Acetyl hypochlorite decomposes readily to carbon dioxide by a free-radical chain process and is a poor chlorinating agent.³⁰ Since methyl chloride formation is significant under any conditions where the hypochlorite is allowed to build up, indications are that reaction 10 is relatively slow. The low yields of chlorobenzene and carbon dioxide from the benzoyl hypochlorite intermediate compared to acetyl hypochlorite³¹ are in keeping with the relative stabilities of benzoyloxy and acetoxy radicals.³²

The dependence of the rate of disappearance of peroxide on the presence of reactive substrates can be accounted for, if the initial reaction (2) between benzoyl peroxide and lithium chloride is considered reversible.³³

(28) P. B. D. DeLaMare, I. C. Hilton, and C. A. Vernon, *J. Chem. Soc.*, 4039 (1960).

(29) The implication that hypochlorous acid is a more selective chlorinating agent compared to benzoyl hypochlorite, and especially *t*-butyl hypochlorite, is intuitively unreasonable.

(30) W. Bockmuller and F. W. Hoffman, *Ann.*, 165 (1935).

(31) Cf. R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956); C. V. Wilson, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 5.

(32) M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 153f.

(33) By reversible we do not imply that reaction 2 is a rapid equilibrium such that equilibrium concentrations of benzoyl hypochlorite are maintained. For purposes of argument, we can consider only reactions 2 and a

reaction such as: $\text{PhCO}_2\text{Cl} + \text{ArH} \xrightarrow{k} \text{PhCO}_2\text{H} + \text{ArCl}$, as operative. If a steady-state assumption is invoked, after the induction period the rate of disappearance of peroxide and the dependence on ArH will be a function

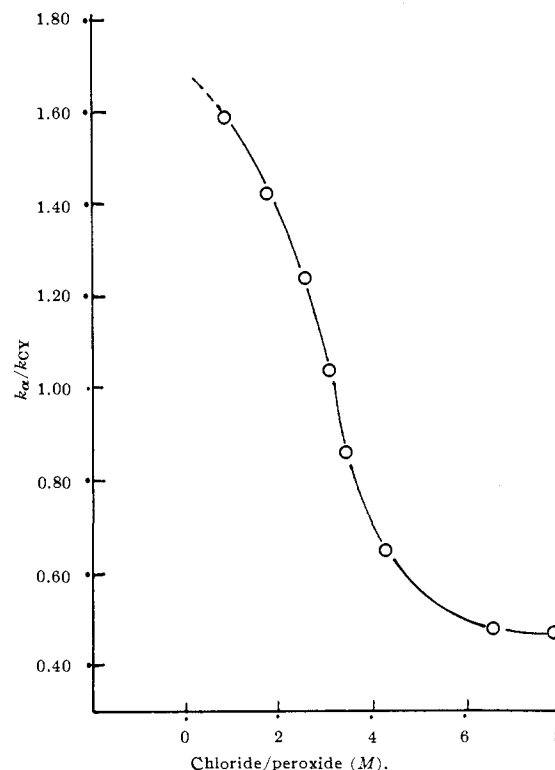
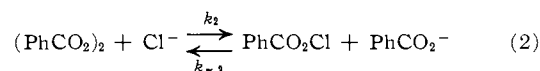


Fig. 3.—Effect of chloride on the relative reactivities of toluene and cyclohexane in chlorinations.



We have re-examined the reaction between lithium benzoate and chlorine in DMF⁴ and dimethyl sulfoxide solutions at low temperatures (10°). Though benzoyl peroxide is stable under these conditions, we could find no evidence for its formation; possibly it can be formed under conditions of the peroxide-lithium chloride reaction.

It is generally recognized³¹ that acyl hypohalites are intermediates in the reaction of silver carboxylates with halogens (Hunsdiecker reaction). There are several instances³⁴ in which electrophilic halogenations (particularly brominations) have been carried out with these reagents. We believe that the most important difference between the hypohalite formed under Hunsdiecker conditions and that formed from the peroxide is attributed to the presence of excess halide in the latter case. The rapid reaction of hypobromites with bromide (reaction 9) reduces the actual concentration of acyl hypobromites in the peroxide reaction such that the predominant species in solution is molecular bromine and no decarboxylation is observed.³⁵

The postulation of benzoyl hypochlorite as the first intermediate in the reaction of benzoyl peroxide and lithium chloride was originally made by Bamford and

of the relative magnitudes of the terms, $k_{-1}(\text{PhCO}_2^-)$ and $k(\text{ArH})$. In the extreme cases, if the latter is large compared to the former, simple second-order kinetics will be observed; the reverse situation will lead to dependence on ArH. Similar kinetics have been observed in the well-studied halogenations of ketones and the reaction of haloforms with bases.

(34) R. A. Barnes and R. S. Prochaska, *J. Am. Chem. Soc.*, **72**, 3188 (1950); W. G. Dauben and N. Tilles, *ibid.*, **72**, 3185 (1950); R. N. Haszeldine and A. G. Sharpe, *J. Chem. Soc.*, 993 (1952); A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1363 (1951); D. E. Janssen, J. Van Allan, and C. V. Wilson, *J. Org. Chem.*, **20**, 1326 (1955).

(35) Studies with *n*-valeryl peroxide and lithium bromide show that the predominant product is bromine and no *n*-butyl bromide is formed (unpublished observations, R. V. Subramanian).

White.⁴ They considered the rate-determining step of the reaction to be the nucleophilic displacement of chloride ion on the peroxidic oxygen (reaction 2). The kinetic results, the evidence for hypochlorite intermediates just adduced, and the reaction with styrene to form a mixture of chloroacetate and benzoate adducts (see Experimental) are in accord with this formulation.

Displacements on peroxides by a variety of nucleophiles have been considered.¹ A linear free-energy correlation of the logarithms of the rates of reaction of halide ions with monosubstituted peroxides in aqueous solution and the base strength (pK_B) of the leaving group has been observed. However, hypohalites as actual intermediates³⁶ in these reactions is more difficult to determine in aqueous solution, since subsequent attack by halide to form molecular halogen is the usual course.³⁷

The use of chloride as a nucleophile in displacements on peroxides is facilitated in nonaqueous solution. Bamford and White's studies in dimethylformamide and our studies in acetic acid and acetonitrile show that chloride can act effectively as a nucleophile. The usual nucleophilic reactivity sequence, $I^- > Br^- > Cl^-$, has been attributed largely to polarizability or related factors.¹ Recently Weaver and Hutchison³⁸ have presented evidence that the differences in nucleophilic reactivity of lithium halides in nonaqueous solution is largely attributed to ion-pair formation, and in some cases chloride is a more effective nucleophile than iodide.

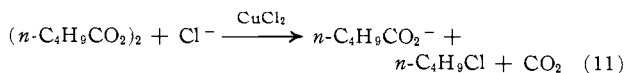
The addition of small amounts of cupric chloride to the reaction system consisting of benzoyl peroxide and lithium chloride is not characteristic of its effect on peroxides generally. With benzoyl peroxide cupric chlo-

(36) For example, it can be postulated that attack of halide ion on peroxide leads directly to a halogen atom as in the reaction: $ROOR' + X^- \rightarrow RO^- + X \cdot + R'O$ [cf. W. K. Wilmarth and A. Haim, ref. 1, p. 192].

(37) Cf. M. C. R. Symons, *J. Chem. Soc.*, 273 (1955); D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).

(38) W. M. Weaver and J. D. Hutchison, *ibid.*, **86**, 261 (1964).

ride has little effect (*vide supra*) other than to inhibit extraneous radical chain processes. With aliphatic diacyl peroxides, on the other hand, cupric chloride has a catalytic effect, especially in the presence of excess halide salts in nonaqueous solutions.³⁹ The stoichi-



ometry of such reactions (11) is different. For example, *n*-valeryl peroxide yields a mole of *n*-butyl chloride, carbon dioxide, and lithium valerate. There is a marked similarity of these reactions to other decompositions of peroxides catalyzed by copper salts,⁵ which all proceed *via* cuprous salt intermediates. In the absence of cupric salts, *n*-valeryl peroxide reacts only very slowly with lithium chloride at temperatures (65°) where the unimolecular thermolysis of the peroxide is a significantly complicating factor. The reaction of valeryl peroxide with lithium bromide is exceedingly rapid and in the presence of cupric salts the two processes^{2,11} occur concomitantly.³⁹

In summary, we have presented evidence that both molecular chlorine and benzoyl (acetyl) hypochlorite formed by reactions 2 and 5 are the principal species responsible for chlorinations in a system comprised of benzoyl peroxide and lithium chloride in acetic acid. With toluene as substrate, the radical chain chlorination (reaction 6, 7) to form benzyl chloride is the preferred reaction in the absence of air or with cupric chloride. The slower electrophilic chlorination of toluene to form nuclear substituted chlorotoluenes⁴⁰ in the presence of inhibitors is attributed to molecular chlorine.²⁷

Acknowledgment.—We wish to thank the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for generous grants which supported this work.

(39) Unpublished results, R. V. Subramanian.

(40) Electrophilic side chain halogenation (cf. E. Baciocchi and G. Illuminati, *Tetrahedron Letters*, **15**, 637 (1962)) is not obtained with toluene.

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Reduction of Organic Halides by Chromium(II). Mechanism of the Formation of Benzylchromium Ion¹

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Benzylchromium ion, $C_6H_5CH_2Cr(H_2O)_5^{+2}$, has been prepared by several independent routes and found to be the same as that formed⁷ during the reaction of benzyl chloride and chromium(II). The kinetics of the formation of this complex ion have been studied and a mechanism proposed which includes the generation of benzyl radicals as intermediates in the reaction. Trapping experiments with acrylonitrile and butadiene are described. The similarity of the slow step of the reaction with atom-transfer reactions involving a bridge-activated complex and the ligand-transfer oxidation of free radicals is discussed. Related aralkylchromium ions have been prepared and their electronic absorption spectra and kinetics of formation studied.

Introduction

It has been known for some time² that chromous ion is a potent and versatile reducing agent for organic

(1) Presented in part at the 1st International Conference on Organometallic Chemistry, Cincinnati, Ohio, June, 1963.

(2) M. Berthelot, *Ann.*, [4] **9**, 401 (1866); W. Traube, *et al.*, *Ber.*, **49**, 1692 (1916); **58**, 2773 (1925); J. B. Conant, *et al.*, *J. Am. Chem. Soc.*, **45**, 2466 (1923); **47**, 1959 (1925); **48**, 1016 (1926); **53**, 676 (1931).

compounds. The reduction of unsaturated functional groups, nitriles, carbonyl-containing compounds, carbonium ions, and organic halides has been summarized recently.³ We have been engaged in the study⁴ of

(3) (a) V. Schwarz, A. Kasal, *Pokroky v organicke synthese*, **4**, 877 (1957); (b) L. H. Slauch and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964); (c) C. E. Castro and W. C. Kray, *J. Am. Chem. Soc.*, **85**, 2768 (1963); (d) K. D. Kopple, *ibid.*, **84**, 1586 (1962).