The Radical-Induced Decomposition of Azides

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Abstract: The few known instances of radical-induced decomposition of azides are reviewed briefly. The decomposition of bis(*o*-azidobenzoyl) peroxide in benzene is found to occur with very little loss of the azide functional groups. A hydrogen atom transfer mechanism is suggested for the small amount of carbazole produced. No decomposition of phenyl azide is induced by benzoyl peroxide in degassed benzene. The decomposition of phenyl azide in CCl_4 is induced by trichloromethyl free radicals. These may be produced either directly by the decomposition of trichloroacetyl peroxide or the *t*-butyl perester, or indirectly by chain transfer from benzoyl peroxide. The major product of the decomposition in CCl_4 in the presence of benzoyl peroxide is *p*-chlorophenylcarbonimidoyl dichloride unaccompanied by any of the *o*-chloro isomer or the unsubstituted analog. The initial rates of azide decomposition are first order with respect to the concentration of the azide, and one-half order with respect to the concentration of benzoyl peroxide.

There is a considerable body of information which we would like to mention briefly that is relevant in some degree to the behavior of azides in the presence of free radicals. For example, it has long been clear from product studies that decomposing azides sometimes themselves give rise to radicals.[1] However, the structural requirements for successful radical attack on the azide are quite special, as is indicated by the rarity of reports of deviation from first-order decomposition kinetics as well as by the negative results of several experiments in which external radical sources were provided.[1c,d] It is a reasonable hypothesis that a triplet state of the nitrene is responsible for the spontaneous radicals. Nitrenes (either singlet or triplet) are frequent, and possibly even universal, intermediates in the decomposition of azides,[2] the evidence for the exceptions being plausible rather than compelling.[2a,c,f] Although the thermal decompositions of azides may be expected to produce the singlet nitrene initially, the ground state has so far invariably been found to be the triplet.[3] Photolysis may produce some triplet nitrene directly[4] and give an enhanced yield of typical radical products.[1c]

The decomposition of sulfonyl and aryl azides has been shown to be accelerated by certain peroxide-derived radicals,[1d,5] by thiyl radicals,[1d] and by 2-hydroxy-2-propyl radicals.[6] The latter reaction is also effective with carbamoyl and ethoxycarbonyl azides.[6]

Bis(*o*-azidobenzoyl) Peroxide

The disappearance of the peroxide function on heating this rather hazardous[7] compound in benzene in the absence of air is approximately first order with rate constants 2.5×10^{-5} sec^{-1} at 50° and 9.4×10^{-4} sec^{-1} at 80°. These constants are for the later parts of the runs, after about the first half-life. The rate constants are somewhat smaller during the first half-life; however, there does not appear to be any dependence of the rate constants on the initial concentrations in the range 5×10^{-3} *M* to 10^{-2} *M*. Because of the explosion hazard with this compound, the apparent autocatalysis was not further explored. It should be noted that these rate constants are of the same order of magnitude as those for the decomposition of other typical bis-*ortho*-substituted benzoyl peroxides in which there is no special participation of the substituent in the rate-limiting step.[8]

The products of the decomposition of a degassed 0.05 *M* solution of the peroxide in benzene at 80° were partially accounted for as *o*-azidobenzoic acid (102 mole %), *o*-azidobiphenyl (18 mole %), phenyl *o*-azidobenzoate (20 mole %), and a mixture of unidentified, apparently aliphatic,[9] esters of *o*-azidobenzoic acid (20 wt % of the peroxide). In addition carbazole was isolated, but only in 10 mole % yield.

Carbazole is the major product obtained in the decomposition of *o*-azidobiphenyl in inert solvents, but the rate of the reaction is so low[10] as to rule it out as the source of the carbazole formed from the azidoperoxide. Of the several remaining explanations for this product, the most plausible is that the radical precursor of *o*-azidobiphenyl undergoes an intramolecular *reductive* radical-induced decomposition of the azide group (eq 3). Equation 3 is somewhat analogous to the reductive decomposition of aryl azides induced by the 2-hydroxy-2-propyl radical,[6] for which a hydrogen atom transfer mechanism has been suggested, giving N_2, ArNH·, and acetone.

The formation of products in which the azide group is intact indicates that the azide functional group will not react during the estimated lifetimes of any of the following radicals: an aroyloxy radical in the same

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[1] (a) A. Bertho, *Ber.*, **57**, 1138 (1924); (b) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961); (c) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, 87, 1947 (1965); (d) T. Shingaki, *Sci. Rept. Osaka Univ.*, **11**, 67, 81 (1963).

[2] (a) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963); (b) G. L. Buchanan and R. M. Levine, *J. Chem. Soc.*, 2248 (1950); J. N. Ashley, G. L. Buchanan, and A. P. T. Eason, *ibid.*, **60** (1957); (c) L. Horner, G. Bauer, and G. Dörges, *Chem. Ber.*, **98**, 2631 (1965); (d) Y. Yukawa and Y. Tsuno, *J. Am. Chem. Soc.*, **79**, 5530 (1957); (e) P. A. S. Smith and J. H. Hall, *ibid.*, **84**, 480 (1962); (f) W. A. Saunders, Jr., and E. A. Caress, *ibid.*, **86**, 861 (1964); (g) L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, **96**, 399 (1963).

[3] (a) E. Wasserman, quoted by J. S. McConaghy, Jr., and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 2357 (1967); (b) G. Smolinsky, E. Wasserman, and W. A. Yager, *ibid.*, **84**, 3220 (1962); (c) G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963); (d) E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 3166 (1964); (e) R. M. Moriarty, M. Rahman, and G. J. King, *ibid.*, **88**, 842 (1966).

[4] J. S. McConaghy, Jr., and W. Lwowski, *ibid.*, **89**, 4450 (1967).

[5] J. E. Leffler and Y. Tsuno, *J. Org. Chem.*, **28**, 902 (1963).

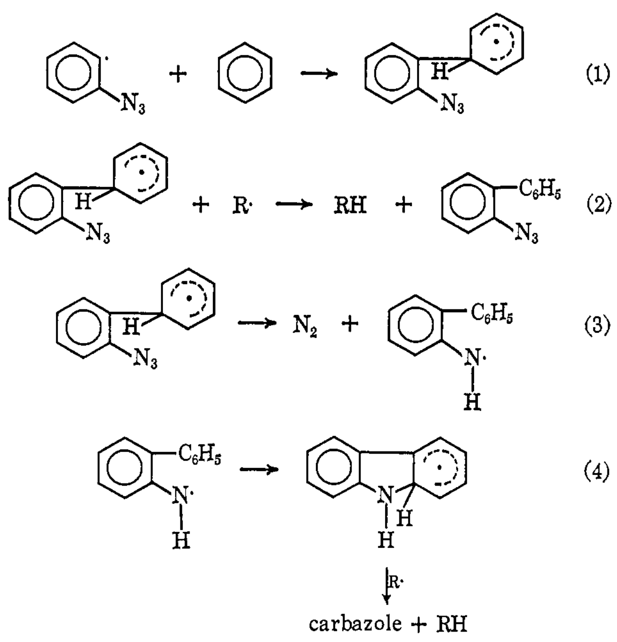
[6] L. Horner and G. Bauer, *Tetrahedron Letters*, 3573 (1966).

[7] A small crystalline sample of this peroxide detonated rather violently when it was touched by a metal spatula, even though previous samples had been handled in much the same way without decomposition.

[8] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).

[9] D. F. Detar, *ibid.*, **89**, 4058 (1967).

[10] P. A. S. Smith, *ibid.*, **84**, 480 (1962).



solvent cage[11] (10^{-11} sec), an aroyloxy radical still close enough for secondary recombination[11] to occur (10^{-9} sec for diffusion beyond the likelihood of return), an *o*-carboxy radical substituent *in the same molecule* (10^{-4} to 10^{-5} sec estimated for decarboxylation),[9] and an unpaired electron in a σ[12] orbital of carbon in the *ortho* position *of the same molecule* (10^{-4} sec for addition to the solvent).[9]

The stability of the *o*-azidophenyl radical, at least for 10^{-4} sec or thereabouts, deserves some additional comment. It is conceivable that there may exist a lower energy, spin-forbidden path for the decomposition of aryl azides in which the triplet nitrene is formed directly. If there is such a reaction path, the azide decomposition should be catalyzed by inhomogeneous magnetic fields. Such a field is present in the *o*-azidophenyl radical because of the unpaired electron. On the other hand, it should be noted that the presence of heavy atoms,[13] which should exert a similar effect, also failed to accelerate the decomposition of either *o*-iodobenzoyl azide[14] or *o*-iodobenzenesulfonyl azide.[15]

Induced Decomposition of Aryl Azides. For comparison with the decomposition of bis(*o*-azidobenzoyl) peroxide in benzene, benzoyl peroxide (0.083 *M*) was decomposed at 80° in a carefully degassed benzene solution of phenyl azide (0.01 *M*). There was no decrease in the azide concentration, as measured by the band at 2120 cm^{-1} in the infrared, during two half-lives of the peroxide. In less carefully degassed solutions, small and variable amounts of azide decomposition were noted.

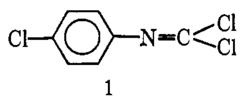
The decomposition of phenyl azide in *carbon tetrachloride* at 79.8° is quite rapid in the presence of benzoyl peroxide, whereas the rate in the absence of initiator is negligible (Figure 1).

Table I. Products from the Decomposition of Phenyl Azide[a] (0.027 *M*) with Benzoyl Peroxide[b] (0.087 *M*) in CCl_4 at 79.8°

Product	Yield,[c] mole %
p-Chlorophenylcarbonimidoyl dichloride[f]	67
Nitrogen[e]	104
Hexachloroethane	43 (40)[d]
Chlorobenzene	137 (100)[d]
Terephthalic acid	9 (32)[d]
Benzoic acid	15 (10)[d]
Chlorophenyl benzoates	1 (11)[d]
Phenyl benzoate	3
Carbon dioxide	138 (135)
Hydrochloric acid	25

[a] 91% decomposed. [b] 100% decomposed. [c] Mole per cent of benzoyl peroxide, except for nitrogen, hydrochloric acid, and *p*-chlorophenylcarbonimidoyl dichloride, for which the yields are mole per cent of decomposed azide. [d] Figures in parentheses are mole per cent of benzoyl peroxide, initially 1.30 *M*, decomposed in the absence of azide.[16] Note the difference in initial peroxide concentrations. [e] A tracer experiment showed that the nitrogen comes exclusively from the outer two N atoms of the azide. [f] No unsubstituted phenylcarbonimidoyl dichloride was present. The upper limit for the *ortho* or *meta* isomers is 1%.

Products (Table I). The products from the decomposition of *benzoyl peroxide* in carbon tetrachloride at 79.8° [16] are very little changed by the presence of phenyl azide (Table I). The major products attributable to the *azide* are nitrogen (from the two outer nitrogen atoms of the azide),[17] *p*-chlorophenylcarbonimidoyl dichloride (structure 1), and HCl.



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A careful search was made for unsubstituted and *o*-chloro-substituted phenylcarbonimidoyl dichloride. Neither of these appears to be present, or if present their yields cannot exceed 1%. There did appear to be one substituted phenylcarbonimidoyl dichloride, but it was found in very small amount. This compound is probably a benzoyloxy derivative.

Since there is no change in the intensity of the anil band at 1650 cm^{-1} when the peroxide is decomposed in a CCl_4 solution of *p*-chlorophenylcarbonimidoyl dichloride, the less than quantitative yield of this substance is not due to destruction by the peroxide. It was also ascertained that there is no reaction between the anil and the azide at 80°. A possible route to the *p*-chlorophenylcarbonimidoyl dichloride is the reaction of phenylcarbonimidoyl dichloride with Cl_2. However, it was found that this reaction (which did not go at all in the absence of benzoyl peroxide) gave considerable amounts of the *ortho* and *meta* isomers, as well as the *para* isomer.

Kinetics

The decomposition of benzoyl peroxide in carbon tetrachloride without other additives is a first-order process at high dilutions, but the presence of induced decomposition can be detected by the dependence of the apparent first-order rate constants on the initial con-

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(11) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

(12) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *ibid.*, **89**, 4875 (1967); G. Porter and B. Ward, *Proc. Roy. Soc.* (London), **A287**, 457 (1965); J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965).

(13) An example of the heavy atom effect is the increased proportion of singlet cyanonitrene converted into the triplet in chlorinated solvents as compared with other solvents: A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).

(14) J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, **25**, 424 (1960).

(15) J. E. Leffler and Y. Tsuno, *ibid.*, **28**, 902 (1963).

(16) Y. Ikeda and M. Wakita, *Bull. Liberal Arts Coll., Wakayama Univ., Nat. Sci.*, **5**, 12 (1955); *Chem. Abstr.*, **49**, 10240 (1955).

(17) Shown by an isotopic tracer experiment.

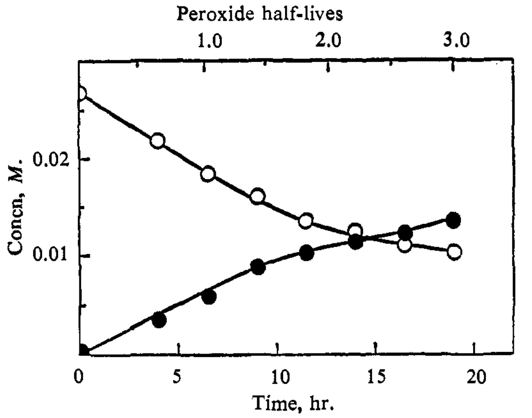

Figure 1. Decomposition of phenyl azide (0.027 *M*) induced by benzoyl peroxide (0.0868 *M*) in CCl_4 at 79.8°: azide concentration (○), *p*-chlorophenylcarbonimidoyl dichloride concentration (●).

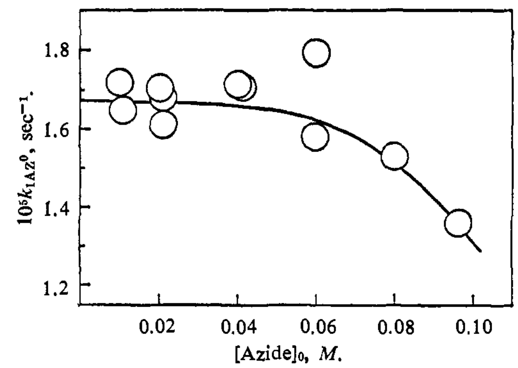

Figure 2. Effect of varied initial azide concentrations on k_{1Az}^0 at a constant initial peroxide concentration of 0.100 *M*.

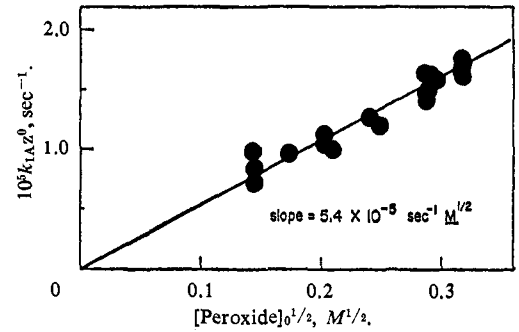

Figure 3. Effect of initial peroxide concentration on k_{1Az}^0 at initial azide concentrations ranging from 0.006 to 0.04 *M*.

centration.[18] At a peroxide concentration of 0.087 *M*, for example, the contribution of a three-halves-order induced decomposition process to the total rate is about 34%. In the presence of various amounts of phenyl azide, the peroxide decomposition rates remained approximately first order and the apparent first-order rate constants were within 10% of the value calculated from the reported first- and three-halves-order rate constants in carbon tetrachloride alone. Since no unusual peroxide-derived products were isolated, it is probable that most of the $CCl_3\cdot$ radicals consumed by the reaction with the azide are replaced in a later step and that there is no appreciable cross-induced decomposition by the azide.

The rates of the benzoyl peroxide accelerated decomposition of the azide in CCl_4 at 79.8° are difficult to reproduce. Careful degassing is necessary since oxygen increases the rate, and it is also necessary to use a freshly distilled sample of the azide uncontaminated by stopcock grease, for example. Even with these precautions, there are occasional runs whose rates may be as much as 100% greater than normal. The progress of the azide decomposition was followed by measuring the intensity of the azide band at 2110 cm^{-1}.

The chain efficiency of the induced decomposition of the azide is low, so that even with an excess of peroxide, the plot of azide concentration against time eventually levels off to the essentially zero rate of the spontaneous azide decomposition at 79.8°. In general, the initial rates are more reproducible than those later in the reaction. We find it convenient to describe the rates in terms of an initial first-order constant, k_{1Az}^0.

Figure 2 shows the results of some of our measurements of k_{1Az}^0 in runs with constant initial peroxide concentrations and variable initial azide concentrations. At initial azide concentrations up to about 0.05 *M*, the value of k_{1Az}^0 is about 1.67×10^{-5} sec^{-1}, independent of azide concentration within experimental error. At higher initial azide concentrations, the rate constant appears to decrease. Judging from the experiments with *o*-azidobenzoyl peroxide and with benzoyl peroxide and phenyl azide in benzene, the attack of phenyl radicals or benzoyloxy radicals on the azide is likely to give substitution in the ring, rather than induce any decomposition of the azide function. It may be that at high concentrations the azide begins to intercept some of the benzoyloxy or phenyl radicals before chain transfer to the solvent can occur.

Figure 3 shows the linear relationship between the initial first-order rate constant for the decomposition of the azide and the square root of the initial peroxide concentration for reaction mixtures in which the azide concentration ranged from 0.006 to 0.040 *M*.

Azobenzene, water, *p*-chlorophenylcarbonimidoyl dichloride, benzoic acid, hexachloroethane, chlorobenzene, and a product solution from a previous run had no effect on the rate of the induced azide decomposition. However, oxygen did have an effect. For example, in an *undegassed* run with initial azide concentration equal to 0.01 and initial peroxide concentration equal to 0.0498, the mean rate constant for the disappearance of the azide was 8.4×10^{-5} sec^{-1}, about seven times the rate appropriate for that initial peroxide concentration in a carefully degassed run.

The Effect of Other Radical Sources in CCl_4. Bis(trichloroacetyl) peroxide[19,20] decomposes rapidly in CCl_4 at room temperature and induces some decomposition of phenyl azide. No *p*-chlorophenylcarbonimidoyl dichloride was produced, however, nor were we able to isolate any substance that might be a precursor of the dichloride. Some HCl was produced. It should be noted that this peroxide is dangerously unstable, and it was not feasible to degas the reaction mixture or to dry it completely.

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(18) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(19) C. Zimmerman, U. S. Patent 2,580,373 (Dec 25, 1951); *Chem. Abstr.*, **46**, 6668c (1952).

(20) W. J. Miller, Jr., *Chem. Abstr.*, **46**, 7989 (1952); *Natl. Nuclear Energy Ser. Div. VII*, **1**, 567 (1951).

The decomposition of *t*-butyl trichloroperacetate[21,22] in CCl_4 at 80° also induces the decomposition of phenyl azide. A product analysis showed hexachloroethane, *p*-chlorophenylcarbonimidoyl dichloride, and *p*-chlorotrichloroacetanilide. The latter compound is probably produced from the reaction of the anil with trichloroacetic acid.[23]

Substituent Effects. Table II shows the decomposition rate constants for variously substituted phenyl azides in 0.083 *M* solutions of benzoyl peroxide in carbon tetrachloride at 79.8°. The initial azide concentrations were all close to 0.01 *M*. The Hammett relationship for these rate constants is improved by using a σ^- value for *p*-carbomethoxy, the only substituent capable of electron-withdrawing resonance effects. The ρ value is -0.98, the correlation coefficient, 0.98. The negative ρ value is in accord with a mechanism in which $CCl_3\cdot$ attacks the azide, since this radical is well known to be electrophilic.[24,25]

Table II

Substituent	$k_{1Az}^0 \times 10^5$ sec^{-1}	Substituent	$k_{1Az}^0 \times 10^5$ sec^{-1}
p-CH_3O	3.2	3,5-Dichloro	0.44
H	1.7	*p*-Carbomethoxy	0.29
m-Cl	0.94	*o*-Methoxy	3.4
m-F	0.66	*o*-*t*-Butyl	0.86

The effects of the two *ortho* substituents in Table II are small, suggesting that the attack is at the outer nitrogen atom.

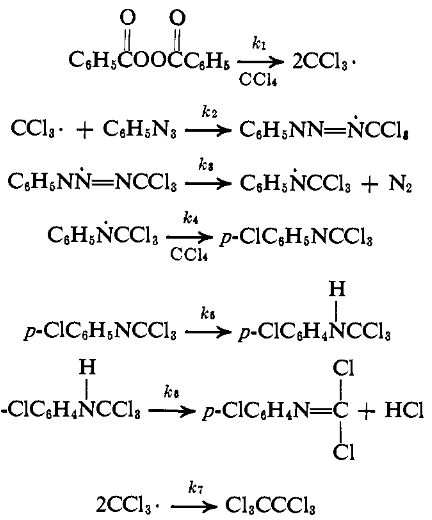
The Reaction Mechanism. The formation of *p*-chlorodiphenylcarbonimidoyl dichloride, and the fact that the empirical rate law has the form of eq 5, suggest that the azide decomposition is induced by $CCl_3\cdot$ which is regenerated in a later step, and that the chain-terminating step is the dimerization of the $CCl_3\cdot$ radicals. Application of the steady-state approximation to Scheme I (and to similar mechanisms) gives an initial rate law of the correct form.

$$\frac{-\mathrm{d}[\mathrm{ArN_3}]}{\mathrm{d}t} = k_\mathrm{d}\left(\frac{k_\mathrm{i}}{k_\mathrm{t}}\right)^{1/2}[\mathrm{P}]^{1/2}[\mathrm{ArN_3}] \tag{5}$$[26]

Scheme I is a simplified scheme with the required properties.

The formation of *p*-chlorophenylcarbonimidoyl dichloride to the *total exclusion* of the *ortho* isomer makes it unlikely that rearrangement of N-chloro-N-trichloromethylaniline is an important reaction path. For example, the Orton rearrangement of N-chloroacetanilide gives a considerable amount of the *ortho* isomer even under free-radical conditions.[27]

Scheme I



$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow[CCl_4]{k_1} 2CCl_3\cdot}$$

$$\mathrm{CCl_3\cdot + C_6H_5N_3 \xrightarrow{k_2} C_6H_5NN{=}\dot{N}CCl_3}$$

$$\mathrm{C_6H_5N\dot{N}{=}NCCl_3 \xrightarrow{k_3} C_6H_5\dot{N}CCl_3 + N_2}$$

$$\mathrm{C_6H_5\dot{N}CCl_3 \xrightarrow[CCl_4]{k_4} \mathit{p}\text{-}ClC_6H_5NCCl_3}$$

$$\mathrm{\mathit{p}\text{-}ClC_6H_5NCCl_3 \xrightarrow{k_5} \mathit{p}\text{-}ClC_6H_4\overset{H}{\overset{|}{N}}CCl_3}$$

$$\mathrm{\mathit{p}\text{-}ClC_6H_4\overset{H}{\overset{|}{N}}CCl_3 \xrightarrow{k_6} \mathit{p}\text{-}ClC_6H_4N{=}\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}} + HCl}$$

$$\mathrm{2CCl_3\cdot \xrightarrow{k_7} Cl_3CCCl_3}$$

An intermolecular reaction of a bulky chlorinating agent such as an N-chloro compound would afford a plausible explanation of the strong directive effect. However, such reagents should chlorinate phenyl azide at least as rapidly as the other possible substrates. *p*-Chlorophenyl azide would not be attacked rapidly by $CCl_3\cdot$ radicals in competition with phenyl azide, and should be a readily detectable product. A control experiment with phenylcarbonimidoyl dichloride showed that this substance is not chlorinated at all under the reaction conditions. In step 4 of Scheme I we have used a reaction of N-trichloromethylanilino radical at its *para* position, which is followed by rearrangement to *p*-chloro-N-trichloromethylaniline in step 6.

Step 6 of Scheme I is supported by the rapid elimination of HCl from analogous Cl_2FC compounds at 0°.[28]

Reaction mechanisms like Scheme I, but elaborated to include provision for the induced decomposition of benzoyl peroxide and the formation of some benzoic acid, can be made to fit the *initial* azide decomposition rates and also the entire course of the disappearance of peroxide. However, two major deficiencies remain: the actual yield of anil is only 67% and the rate of disappearance of azide later in the run is much faster than predicted if rate constants for the individual steps are chosen in such a way as to give the correct *initial* rate constants. Since neither the addition of the known products nor of a crude product mixture increased k_{1Az}^0, we conclude that the autocatalysis must be due to an intermediate, possibly the *p*-chloro-N-trichloromethylaniline, suggested in Scheme I as a precursor for the anil. We hesitate to propose a detailed reaction scheme involving this intermediate, but its share of the induced decomposition might be responsible for the 33% of the C_6H_5N structures unaccounted for in the products and for the unusually high yield of benzoic acid.

Experimental Section

Bis(*o*-azidobenzoyl) Peroxide. *Caution*, see footnote 7. A 40% excess of $SOCl_2$ was added to 3 g (0.018 mol) of *o*-azidobenzoic acid in 30 ml of benzene and the mixture refluxed for 90 min with exclusion of moisture. After complete stripping of solvent *in vacuo*, the crude acid chloride was dissolved in 4 ml of toluene and added during 20 min to a stirred solution of 1.0 g of Na_2O_2 in 10 ml of H_2O at 2°. After further stirring at 2° for 90 min, the reac-

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(21) C. Rüchardt and R. Hecht, *Chem. Ber.*, **98**, 2466 (1965).

(22) P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.*, **82**, 1753 (1960).

(23) J. B. Murphy, *J. Org. Chem.*, **29**, 1613 (1964).

(24) J. I. G. Cadogan and D. H. Hey, *Quart. Rev.* (London), **8**, 308 (1954).

(25) M. S. Kharasch, E. Simon, and W. Nudenberg, *J. Org. Chem.*, **18**, 328 (1953).

(26) In eq 5, k_d is the rate constant of a bimolecular reaction of $CCl_3\cdot$ with the azide, k_i is the first-order rate constant for formation of the initiating radicals, and k_t is the rate constant for the termination step.

(27) K. N. Ayad, C. Beard, R. F. Garwood, and W. J. Hickenbottom, *J. Chem. Soc.*, 2981 (1957); J. Coulson and G. H. Williams, *ibid.*, *B*, 174 (1967).

(28) K. A. Petrov and A. Neimysheva, *J. Gen. Chem. USSR*, **29**, 2135 (1959).

tion mixture was allowed to come to room temperature and the crude peroxide (2.13 g, 73% yield) removed by suction filtration and washed with cold water. The crude product melted at 101–102° (capillary inserted in block at 90°). The optimum method of recrystallization is to dissolve a small amount of the peroxide in 5 ml of 95% ethanol preheated to 65° and allow it to crystallize at room temperature for 2 hr shielded from light. The recrystallized material melted at 108.5–109°. This peroxide is soluble (at 25°) in benzene, slightly soluble in ethanol and in CCl_4, insoluble in *n*-hexane.

After the explosion hazard was noted, the following procedure was used to prepare solutions of the peroxide. Operating from behind a shield, and using tongs for any necessary manipulations, the mass of crude peroxide from 2.5 g of the acid was separated from the reaction mixture solvent by decantation and gently moved by means of a hooked glass rod onto a sintered-glass funnel attached to a 200-ml vacuum flask. It was then washed with 25 ml of water and covered with 75 ml of 95% ethanol preheated to 60°. After allowing the resulting solution to cool for 2 hr, the ethanol was sucked into the receiver, the funnel covered with an adaptor, and dry air aspirated through the crystalline peroxide for 10 min. Any traces of solid peroxide on the lower part of the funnel were removed by washing with acetone followed by benzene. The crystals were then dissolved in 90 ml of benzene, and the solution was filtered by suction into a fresh receiver. This solution may be washed with $NaHCO_3$ and dried over $MgSO_4$ without loss of titer. It is only moderately sensitive to light.

Decomposition rates in degassed benzene at 88° were measured by following the decrease in intensity of the peroxide band at 1772 cm^{-1}.

Solvent. Reagent grade CCl_4 was stirred with aqueous 20% KOH at 50° for 30 min, then washed with dilute H_2SO_4 and with water. It was dried over $CaCl_2$, then over $MgSO_4$, and finally distilled from P_2O_5 through a 3-ft column.

Benzoyl Peroxide. Commercial benzoyl peroxide was recrystallized several times from chloroform solution by addition of methanol and freed from solvent by pumping the vapors into a trap cooled by liquid nitrogen. The oxidizing power of all samples was at least 99.7% of the theoretical value.

Azides. The azides were synthesized by the reaction of the corresponding diazonium salt with hydrazoic acid by the general method of Smith and Brown[29] with variations[30] in the case of azides that did not crystallize readily. *o*-Methoxyphenyl azide[31] was isolated as a yellow oil, bp 49° (0.5 mm). *m*-Fluorophenyl azide was provided by R. D. Temple.[32] 3,5-Dichlorophenyl azide[30] was crystallized from ethanol, mp 29–30°. Methyl *p*-azidobenzoate was crystallized from ethanol, mp 32.8–34° (lit.[31] 39–40°). 2-*t*-Butylphenyl azide was obtained as a liquid, bp 65° (9 mm), by the diazotization of *o*-*t*-butylaniline, bp 79–80° (3 mm).

Phenylcarbonimidoyl Dichloride and *p*-Chlorophenylcarbonimidoyl Chloride. These compounds were prepared by chlorination of phenyl isothiocyanate.[23]

Trichloroacetanilides. Trichloroacetanilide and its *p*-chloro derivative were prepared by the reaction of trichloroacetic acid with the corresponding phenylcarbonimidoyl dichloride.[33]

***t*-Butyl Trichloroperacetate.** Cl_3CCOCl (5.4 g, 0.030 mol) in 30 ml of pentane was added dropwise, with stirring, to 5.0 g (0.055 mol) of *t*-butyl hydroperoxide and 2.4 g (0.030 mol) of pyridine in 60 ml of pentane at 0°. After an additional 2 hr of stirring at 0°, the reaction mixture was poured over 300 g of ice and washed twice with 50-ml portions of cold 10% HCl. The pentane layer was dried over $MgSO_4$ after washing with 7% $NaCO_3$, then partially stripped of solvent, put onto a Florisil column, and eluted with hexane. The Florisil treatment is to remove residual *t*-butyl hydroperoxide.[22] Removal of solvent left a clear oil having a single sharp carbonyl peak at 1795 cm^{-1}.

Trichloroacetyl Peroxide.[19] Sodium peroxide (2.8 g, 0.036 mol) was added to a solution of 10.0 g of NaCl in 50 ml of H_2O at −20°. To the resulting solution 9.0 g (0.05 mol) of trichloroacetyl chloride was added dropwise, with stirring, over a period of 10 min at −20 to −25°. Optimum yields were obtained when vigorous mechanical stirring was employed and the reaction mixture filtered through a chilled filter within 30 sec after completion of the addition. The solid peroxide was then washed with chilled 5% $NaHCO_3$ and with H_2O, after which it was taken up in 35 ml of CCl_4 precooled to 0°. The CCl_4 solution was dried over $MgSO_4$ before use and filtered through a chilled funnel. This peroxide has a half-life of about 10 min in solutions at 0° and the solid explodes at room temperature.

Analyses. Peroxide was titrated by the method of Wibaut, *et al.*[34]

Azide concentrations were determined by means of the 2110-cm^{-1} infrared band, diluting when necessary, and using the general procedures of Bartlett and Minato.[35]

Products. Products were separated by adsorption chromatography on Florisil (magnesium aluminum silicate), eluting with hexane, and by vapor phase chromatography using Carbowax or Chromosorb. *p*-Chlorophenylcarbonimidoyl dichloride was identified by infrared and nmr and by hydrolysis to *p*-chloroaniline. The absence of the *o*-chloro isomer was checked by control experiments which showed that it would have been separated readily under the vpc conditions used.

The *ortho* isomer was also found to survive the reaction conditions when added to the initial reaction mixture, as was the unsubstituted anil. The *para* isomer was found to be stable in the presence of phenyl azide alone or benzoyl peroxide alone in CCl_4 at 80°.

A mass spectrographic analysis was carried out on the N_2 formed by the reaction of labeled phenyl azide with benzoyl peroxide in CCl_4. The label consisted of 15% ^{15}N at the nitrogen atom adjacent to the ring. The evolved nitrogen had a content of $^{14}N-^{15}N$ of 0.7% as compared to the 0.72% natural abundance.

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