[Contribution from Department of Chemistry, Florida State University]

The Decomposition of Bis(*o*-iodophenylacetyl) Peroxide

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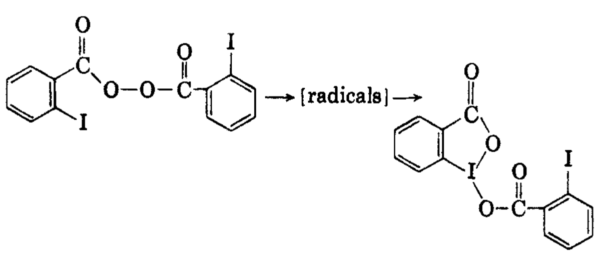
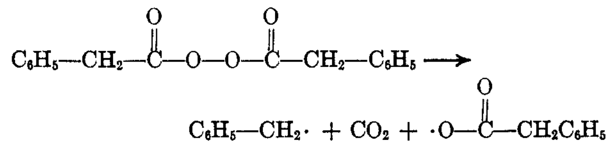
Unlike bis(*o*-iodobenzoyl) peroxide, bis(*o*-iodophenylacetyl) peroxide decomposes without any apparent participation by the iodo substituents. Its decomposition produces radicals capable of initiating vinyl polymerization. The decomposition can also take a polar, acid-catalyzed path; the acid catalysis constants are extremely sensitive to changes in solvent. The rates and products of the decomposition reactions resemble those for the decomposition of bisphenylacetyl peroxide. The behavior of various other iodo-substituted compounds is reported briefly.

The iodo substituents in bis(*o*-iodobenzoyl) peroxide[1] and in *t*-butyl *o*-iodoperbenzoate[2] markedly accelerate the decomposition of those compounds, apparently by a free radical analog of the neighboring group effect.

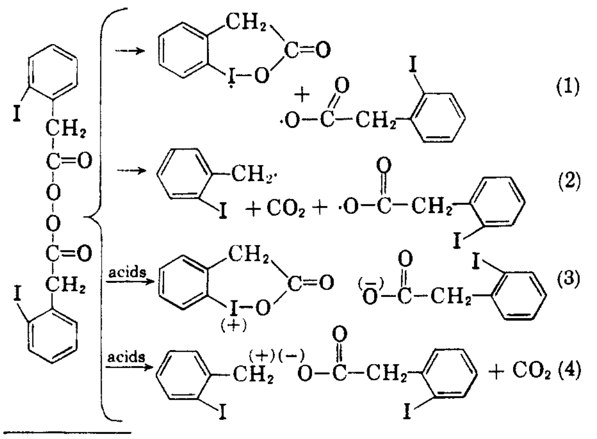


Bis(phenylacetyl) peroxide is also exceptionally unstable, apparently because of its ability to form a molecule of carbon dioxide and a resonance-stabilized benzyl radical in a concerted process,[3] and is sensitive to acid catalysts.



$$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_2-C_6H_5 \longrightarrow C_6H_5-CH_2\cdot + CO_2 + \cdot O-\overset{O}{\overset{\|}{C}}-CH_2C_6H_5$$

Bis(*o*-iodophenylacetyl) peroxide is also very unstable. By analogy with the peroxides previously studied several paths appear plausible for the rate determining step:



Each of these processes involves a lowering of the energy of activation due to resonance or to the incipient formation of new bonds; in each case the lowering of the activation energy would be to some extent counteracted or even outweighed entirely by the corresponding resonance entropy.[4] As far as can be seen from an examination of molecular models, processes involving an even larger number of simultaneous changes in the bonding of the iodo and carboxy groups might also be possible. However, the prediction of the activation entropy for such multiply concerted processes is complicated by the fact that the entropy associated with the rotation about any given bond axis depends on the radius of gyration; it therefore depends on the configuration of the rest of the molecule and hence on the extent to which rotation about any of the other bonds is restricted by the process of activation. We therefore can not predict which of the several processes would have the lowest activation free energy and the greatest rate even though it is clear that the most highly concerted process would have the lowest activation energy.

The kinetics and products of the reaction. Table I shows the principal products of the reaction in various solvents in the absence of added acids. These are consistent with Equation 2 for a concerted formation of carbon dioxide, an iodobenzyl radical, and an iodophenylacetoxy radical. The decomposition of the peroxide initiates the polymerization of vinyl monomers. No cyclic trivalent iodine compound analogous to that formed in the decomposition of bis(*o*-iodobenzoyl) peroxide was observed. The first order rate constants (Table II) are close enough to those for the decomposition of the unsubstituted bis(phenylacetyl) peroxide to make participation by the iodo substituent in the rate-determining step highly unlikely.

The decomposition of the peroxide in the presence of acids is somewhat less accelerated than in the case of bis(phenylacetyl) peroxide. The products of decomposition in the presence of a strong acid

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(1) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

(2) J. C. Martin and W. G. Bentrude, *Chem. and Ind.*, 192 (1959).

(3) P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950).

(4) "Resonance entropy" is a convenient term for the entropy loss associated with the special, relatively static configurations required for resonance or for orbital overlap.

TABLE I

Solvent and Conditions	Product	Mole %, Product/Peroxide	Recovery % Benzyl Groups	Recovery % Carbonyl Groups
Acetone, 0° air present[a]	2,2′-Diiododibenzyl	21 to 22; (26)[a]	21 (26)[a]	
	o-Iodobenzyl alcohol[b]	68 to 78 (52)[a]	37 (26)[a]	
	o-Iodobenzyl *o*-iodophenylacetate[b]	0; (15)[a]	0 (15)[a]	
	o-Iodophenylacetic acid	68; (46)[a]	34 (23)[a]	
		Total	82[b] (90)[a,b]	
Toluene, 0°, N_2 atmosphere	2,2′-Diiododibenzyl	42	42	
	o-Iodobenzyl alcohol[b]	17 to 20	9	
	o-Iodobenzyl *o*-iodophenylacetate[b]	27	27	13.5
	o-Iodophenylacetic acid	2 to 3	1	1
	Carbon dioxide	139 to 143	—	70
		Total	79[b]	84
Chloroform, 0°, N_2 atmosphere	2,2′-Diiododibenzyl	28	28	
	o-Iodobenzyl alcohol[b]	41	20.5	
	o-Iodobenzyl *o*-iodophenylacetate[b]	18	18	
	o-Iodophenylacetic acid	9	4.5	
		Total	71[b]	
Thionyl chloride, 0°, air present	2,2′-Diiododibenzyl	0	0	
	o-Iodobenzyl chloride	84	42	
	o-Iodobenzyl alcohol	3.8	2	
	o-Iodobenzyl *o*-iodophenylacetate	5.1	5	
	o-Iodophenylacetic acid	3.4	2	
		Total	51	
Toluene, 0.2*M* trichloroacetic acid, N_2 atmosphere	Carbon dioxide	93	—	47

[a] Yields from a run in which air was carefully excluded. [b] Some of the *o*-iodobenzyl alcohol is formed during the isolation of the ester, which partially hydrolyzes during chromatography on alumina. The acid moiety of the ester remains on the alumina and is not recovered.

appear to be largely carbon dioxide and *o*-iodobenzyl *o*-iodophenylacetate rather than *o*-iodobenzyl esters of the catalyzing acid. Some *o*-iodophenylacetic acid and some iodobenzyl alcohol were isolated, the latter probably because of partial hydrolysis of the ester on the alumina column. In dichloroacetic acid as a solvent and catalyst the *o*-iodobenzyl *o*-iodophenylacetate formed is readily isolated in pure form; in benzene or toluene in the presence of trichloroacetic acid the quantitative isolation of the pure ester is much more difficult. However, the oils accompanying the ester in the experiment in toluene appear to be largely *o*-iodobenzyl *o*-iodophenylacetate both on the basis of their hydrolysis products and on the basis of their infrared spectrum. The yield of carbon dioxide in the acid-catalyzed reaction in toluene is close to one mole per mole of peroxide. The amount of polystyrene produced by the decomposition of the peroxide in styrene in the presence of 0.05 molar trichloroacetic acid is only about one quarter of that produced in styrene without added acid, indicating that the acid-catalyzed decomposition probably goes by way of a non-radical mechanism.

Table II gives the first order rate constants for the decomposition of the peroxide in various media at 0°. The reaction is first order within a given run. However, increases in the initial peroxide concentration, at least in chloroform, slightly increase the rate constant. As in the case of bis(phenylacetyl) peroxide, there is some induced decomposition. Fig. 1 shows a first order plot of the data for a typical run in chloroform.

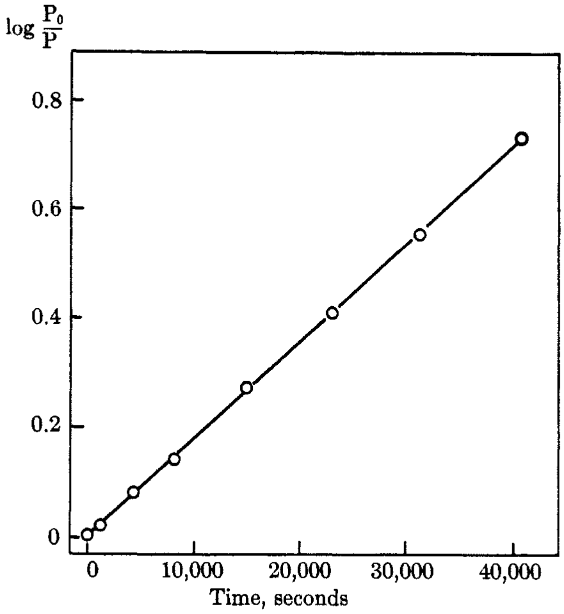

Fig. 1

The decomposition of bis(*o*-iodophenylacetyl) peroxide is also subject to acid catalysis. In toluene at 0° the catalysis constants for trichloroacetic acid are such that the acid-catalyzed part of the decomposition should amount to about 40% in the

TABLE II

Medium	Initial Peroxide Concentration, *M*	*k* (sec^{-1} at 0°) × 10^5
Chloroform	0.0204	3.98
	.035	4.19
	.105	4.14
	.152	4.67
	.212	4.49
Chloroform with		
0.232*M* benzoic acid	0.21	4.19
0.216*M* trichloroacetic acid	.16	7.8
Toluene	0.1	1.30
Toluene with		
0.089*M* trichloroacetic acid	0.1	8.66
0.165*M* trichloroacetic acid		15.2
0.185*M* trichloroacetic acid		19.1
Acetone	0.1	2.60
Acetone with		
0.296*M* trichloroacetic acid	0.098	2.60

presence of 0.01*M* trichloracetic acid. The data available for bis(phenylacetyl) peroxide in the same solvent (but at 18°) correspond to 80% decomposition by the acid-catalyzed process in the presence of 0.01*M* trichloroacetic acid.[3]

The acid-catalysis of the decomposition of bis-(*o*-iodophenylacetyl) peroxide is strikingly dependent on the solvent. Thus in chloroform the rate is increased by less than a factor of two by 0.216*M* trichloroacetic acid while in acetone not even 0.296*M* trichloroacetic acid has a detectable effect. The proportions of acid-catalyzed decomposition in the presence of 0.01*M* trichloroacetic acid in the three solvents would be: toluene, 40%; chloroform 3%; acetone, zero or <0.2%. The reaction in toluene in the absence of added acid shows no auto-catalysis in spite of the greater efficiency of the acid-catalyzed reaction in that solvent; however, the amount of acid produced in toluene is exceptionally low (Table I). The suppression of polymerization by trichloroacetic acid in styrene is consistent with a fast acid-catalyzed decomposition of the peroxide in that solvent. The lack of such an effect by trichloroacetic acid in acrylonitrile suggests that acid catalysis is very slight in acrylonitrile, just as it is in acetone.

The effect of iodo substituents in other reactions. In connection with our experiments on bis(*o*-iodophenylacetyl) peroxide we had occasion to examine briefly the reactions of various other iodo compounds.

Gentle heating of 4-*t*-butyl-2,6-diiodophenol with benzoyl peroxide in benzene produces a transient blue color, probably because of the aryloxy free radical.[5] The blue color fades and is replaced by red, but no quinonoid product is readily isolable from the reaction mixture.

Diazomethyl *o*-iodophenyl ketone is readily converted into *o*-iodophenylacetic acid or its ethyl ester by means of the Wolff reaction with no observable diversion to products attributable to participation by the iodo substituent.

The rearrangement of *o*-iodobenzoyl azide and the Hofmann reaction of *o*-iodobenzoyl amide also proceed in the normal way.

Attempted preparation of *t*-butyl *o*-iodophenylperoxycarbamate from the isocyanate[6] gave a yellow oil which always decomposed violently during chromatography just as the bands began to separate and while they were still near the top of the alumina column. The reaction of the isocyanate with perbenzoic acid gave a complex mixture from which was isolated *o*,*o*′-diiodoazobenzene.

EXPERIMENTAL

Diazomethyl o-iodophenyl ketone. The procedure of Newman and Beal[7] for the preparation of diazoketones was used. The diazomethyl *o*-iodophenyl ketone crystallized during removal of the ether; it was often accompanied by a viscous oil, m.p. 60–61° after two recrystallizations from carbon tetrachloride. Additional product could be obtained by chromatography of the mother liquor, yield 60%.

o-Iodophenylacetic acid and methyl ester. To 32.2 g. of the diazo ketone in about 250–300 cc. of absolute methanol at room temperature was added with stirring a solution of 3 g. of silver benzoate in 31 g. of triethyl amine over a period of 1 to 2 hr. After filtration and removal of the methanol, the liquid residue was dissolved in ether, washed with water, dried over magnesium sulfate, and distilled. Yield of methyl ester, 29.0 g., b.p. 114° at 1.5 mm. The ester was hydrolyzed by warming with 5*N* alkali containing a little alcohol and the acid purified by precipitation from sodium bicarbonate solution after extraction from ether. The acid melted at 117° after recrystallization from aqueous methanol.[8] Equivalent weight: Calcd., 262.1; found 262.4.

o-Iodophenylacetyl Chloride. The acid was heated for 1 hr. at 40° or below with a 25% excess of pure thionyl chloride. After removal of the thionyl chloride at the water pump the acid chloride was distilled, b.p. 145° at 15 mm. The thionyl chloride was first distilled from about 1/5 its volume of quinoline, then from about 2/5 of its volume of linseed oil.

Bis(o-iodophenylacetyl) Peroxide.[9] The acid chloride, 1.12 g., 30% hydrogen peroxide, 0.92 g., and a solution of 0.8 g. sodium hydroxide in 2 cc. of water were cooled in an ice bath. First the cold hydrogen peroxide and then the cold sodium hydroxide solution were added to the cold acid chloride. The mixture was then stirred in an ice bath until no trace of the liquid acid chloride remained and the white, crystalline peroxide had precipitated. The product was

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[5] *Cf.* C. C. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, **78**, 3797 (1956); I. E. Mueller, K. Ley, and W. Keidaisch, *Ber.*, **88**, 1819 (1955); G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

[6] For the general behavior of peroxycarbamates see E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **79**, 6238 (1957).

[7] M. S. Newman and P. Beal, III, *J. Am. Chem. Soc.*, **71**, 1506 (1949).

[8] W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 487 (1941) report 114°.

[9] Preparation of the peroxide on a larger scale is not recommended.

shaken with chloroform precooled to below 0° for a few seconds until the peroxide dissolved. The solution was then transferred to a larger flask and cooled in Dry Ice–acetone to freeze out the water. The ice and other solids were washed with more cold chloroform and the combined chloroform extract quickly washed with cold sodium bicarbonate in a separatory funnel. The remaining traces of the aqueous layer were again removed by cooling in a Dry Ice-acetone bath, the solution filtered, and concentrated in vacuum below 0° to a volume of 15–20 cc. Cold methanol was then added. If the peroxide did not precipitate at this point removal of solvent in vacuum was continued until precipitation occurred. The solid peroxide (kept at or below 0°) was recrystallized from chloroform by adding methanol, both solvents being at 0°.

The peroxide may be dried *in vacuo* at 0°, but it decomposes explosively at room temperature. The yield was about 40%. The filtered and dried material usually assayed about 80% regardless of the number of recrystallizations. This may be due either to an unavoidable but reproducible amount of decomposition during the crystallization or, less probably, to a tendency for a certain proportion of the peroxide to decompose during the analysis. Peroxide determinations were carried out by adding the solid peroxide (or a 1 ml. aliquot from a kinetic run) to an excess of sodium iodide in acetone, diluting with water, and titrating the iodine to a starch end-point with sodium thiosulfate solution.

The decomposition of bis(o-iodophenylacetyl) peroxide. Unless otherwise specified in the tables, the peroxide was decomposed in 20–25 cc. of degassed solvent. A stream of prepurified nitrogen was passed through the solvent to protect the reaction mixture from contamination with air during the addition of the peroxide or the removal of samples. Temperature control was by means of a bath of crushed ice and water. The peroxide was dried *in vacuo* at a low temperature before addition to the reaction mixture. Aliquots for analysis were removed by means of a precooled pipet.

Polymerization initiation by bis(o-iodophenylacetyl) peroxide. A solution of 0.255 g. of bis(o-iodophenylacetyl) peroxide in 13.3 g. of freshly distilled and degassed styrene contained 1.5 g. of polystyrene after decomposition at 0°. A solution of 0.217 g. of the peroxide in 13.0 g. of styrene and 0.12 g. of trichloroacetic acid yielded 0.36 g. of polymer under the same conditions. The polystyrene was isolated by precipitation from ether on addition of methanol. A solution of 0.425 g. of the peroxide in 11.6 g. of acrylonitrile at 0° became turbid in a few minutes and solid in about 1 hr. Similar results were obtained in the presence of the peroxide plus 0.1 g. trichloroacetic acid in acrylonitrile.

Decomposition products from bis(o-iodophenylacetyl) peroxide. Carbon dioxide was swept from the solution of the decomposing peroxide at 0° by a stream of nitrogen. Water and solvent vapor were removed by means of a Dry Ice trap and a magnesium perchlorate tube and the carbon dioxide trapped and weighed in a tube containing ascarite. For the isolation and estimation of the nonvolatile products the reaction mixtures after removal of the solvent were extracted with sodium bicarbonate; the o-iodophenylacetic acid recovered was identified by its melting point. The neutral residue was then further separated by elution chromatography on alumina, in most cases giving three main fractions: o,o'-diiododibenzyl, o-iodobenzyl o-iodophenylacetate, and o-iodobenzyl alcohol.

o,o'-Diiododibenzyl. This substance was the first product to be eluted from the alumina column, coming off with 20% benzene–80% hexane. M.p. after recrystallization from methanol, 101.5–102°.

Anal. Calcd. for $C_{14}H_{12}I_2$: C, 38.73; H, 2.79; I, 58.48, mol. wt. 434. Found: C, 38.98; H, 2.81; I, 58.24; mol. wt. 514 (camphor).

The melting point was not depressed on mixing with a sample synthesized by treating o-iodobenzyl bromide with magnesium in benzene.

o-Iodobenzyl o-iodophenylacetate. This substance was the second to be eluted from the alumina column and came off with 40% benzene–60% hexane. After recrystallization from hexane it melted at 85.5–86°.

Anal. Calcd. for $C_{15}H_{12}O_2I_2$: C, 37.68; H, 2.53; I, 53.09. Found: C, 38.25; H, 2.65; I, 52.77.

Saponification gave the acid and alcohol, identified by their melting points and mixed melting points. The ester was partly hydrolyzed during chromatography on alumina: 0.048 g. put on the column gave on elution 0.034 g. of the recovered ester plus 0.0032 g. of the alcohol.

o-Iodobenzyl alcohol. This substance was eluted from the column with 10% ether–90% benzene. After recrystallization from hexane and from methanol-water it melted at 90.7–91.1°.

Anal. Calcd. for C_7H_7IO: C, 35.9; H, 2.88; I, 54.1, mol. wt. 234. Found: C, 35.88; H, 3.01; I, 54.04; mol. wt. 246 (camphor). The melting point was not depressed by a sample synthesized by hydrolyzing o-iodobenzyl bromide.

N,N'-Bis(2-iodobenzoyl)hydrazine. This substance was formed during the attempted preparation of 2-iodobenzoylhydrazine from the acid chloride and hydrazine hydrate. After recrystallization from ethanol, it melted at 267°.

Anal. Calcd. for $C_{14}H_{10}O_2I_2N_2$: C, 34.17; H, 2.05; N, 5.69; I, 51.58. Found: C, 33.73; H, 1.70; N, 6.19; I, 50.50.

o-Iodobenzoyl azide. The azide was prepared from o-iodobenzoyl chloride and sodium azide in aqueous acetone following the general procedure of Smith.[10] The azide was an oil which slowly evolved nitrogen and solidified at room temperature and which on one occasion inflamed spontaneously.

N,N'-Bis(o-iodobenzoyl)urea. This substance was formed from the wet o-iodobenzoyl azide on standing. After recrystallization from acetone it melted at 232.5° dec.

Anal. Calcd. for $C_{13}H_{10}I_2N_2O$: C, 33.65; H, 2.17; N, 6.04; I, 54.70. Found: C, 33.49; H, 2.22; N, 6.17; I, 54.29.

Ethyl N-o-iodophenylcarbamate. This substance was formed by treating the crude o-iodobenzoylazide reaction mixture with a large excess of ethanol. Sodium chloride was removed by filtration, most of the ethanol was distilled and the urethane precipitated by adding water. After two crystallizations from 50% aqueous ethanol, it melted at 50.5°.

Anal. Calcd. for $C_9H_{10}INO_2$: C, 37.14; H, 3.46; N, 4.81; I, 43.6. Found: C, 37.43; H, 3.66; N, 4.71; I, 43.26.

t-Butyl N-o-iodophenylperoxycarbamate. The general method of O'Brien, Beringer, and Mesrobian was used.[6] Freshly prepared o-iodobenzoylazide (0.01 mole) was separated from the aqueous acetone by addition of water and decantation. It was then treated with 0.01 mole or less of t-butyl hydroperoxide in benzene. Nitrogen was slowly evolved during about 1 hr. and the solution turned yellow. Concentration of the solution *in vacuo* gave a precipitate of N,N'-bis(o-iodophenyl)urea and a yellow oil. Chromatography of the oil on neutral alumina in petroleum ether caused a violent reaction with ejection of the alumina just as the bands were beginning to separate. Elution of the alumina with petroleum ether after the decomposition gave a red-brown tar. A variation of the experiment in which the azide was permitted to rearrange to isocyanate before the t-butyl hydroperoxide was added gave similar results, as does the use of basic alumina. Chromatography on magnesium sulfate did not separate the mixture.

o,o'-Diiodoazobenzene. A similar experiment using perbenzoic acid in chloroform instead of t-butyl hydroperoxide in benzene gave a rapid reaction on adding a few drops of pyridine. The solution turned red, then black, and became hot. The product was a complex mixture which gave a large number of bands on chromatography on neutral alumina. The first fraction (eluted with benzene) gave red needles, m.p. 151.5–152.5° from methanol. Recrystallization from ethanol lowered the melting point; recrystallization from ether gave a product melting at 149.8–150.5°.

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(10) P. A. S. Smith, *Org. Reactions*, Vol. III, p. 387.

Anal. Calcd. for $C_{12}H_8N_2I_2$: C, 33.21; H, 1.86; N, 6.46. Found: C, 32.96; H, 1.57; N, 6.64.

Hofmann reaction of o-iodobenzamide. To a solution of 0.06 cc. of bromine in 0.24 g. of sodium hydroxide and 2 cc. of water, prepared at 0°, was added 0.24 g. of powdered *o*-iodobenzamide. The mixture was stirred for 20 min. at 0°; most of the benzamide dissolved. Stirring was continued in the ice bath for another 1.5 hr., then the mixture was allowed to stand at room temperature for 1 hr. After decanting from a very small undissolved residue the mixture was heated at 80° for 2 hr. On cooling, the *o*-iodoaniline crystallized, m.p. 54–56°, yield 0.20 g.; acetyl derivative, m.p. 109.5–110.5°.

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TALLAHASSEE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Addition of Halogens and Halogen Compounds to Allylic Chlorides. III. Relative Rates of Halogen Addition to Allylic Chlorides

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The magnitude of the deactivation of an ethylenic double bond by electron-attracting groups varies with the type, number, and position of the substituents. Thus, the relative reactivity toward addition of halogen decreases in the order: propene > allyl chloride > 3,3-dichloropropene > 3,3,3-trichloropropene. Isomers of the di- and trichloropropenes containing vinylic halogen were found to be less reactive. Allylic halides were found to add halogen approximately one thousand times faster than the corresponding vinylic halides.

Parts I and II of this series[2] described the additions of halogen compounds to allylic chlorides. This paper is concerned with a study of halogen addition to allylic chlorides. The influence of substituents on the rate of the addition of bromine to ethylenic compounds was investigated by Ingold and Ingold[3] and by Anantakrishnan and Ingold.[4,5] A competitive bromine addition method was used in the presence of methylene chloride at −35° and −78°. The reduced velocity for each ethylenic compound was obtained by comparing the rate of bromine addition of the compound with that of ethylene as unity,[5] *e.g.*, ethylene, 1.0; propene, 2.0; isobutylene, 5.5; trimethylethylene, 10.4; tetramethylethylene, 14.0.

Swedlund and Robertson[6] examined the rate of halogen addition to halogen derivatives of ethylenes. Chlorine was used instead of bromine for the determination of the relative rates which were obtained by comparing the k_2 values calculated at X = 50% (X = halogen absorption). The k_2 values were calculated from the curves by plotting the percentage of halogen absorption against time. The original values were revised in one of their later papers,[7] based on a new value for allyl bromide of 1.3×10^{-2} instead of 3×10^{-1}. (The revised values are included in Table II.)

This study was undertaken to investigate the influence of the number and position of electron-attracting substituents upon the reactivity of the double bond. The methods of preparation for the allylic chlorides used are given in Part I of this series. The kinetic method of Swedlund and Robertson[6] was employed for the rate studies. Vinyl bromide was used as the reference compound to correlate the data of this study with the values on relative rate given in their papers. Except for allyl chloride, chlorine was used instead of bromine to measure the rates of addition. In this type of study, iodine and its compounds are used for the determination of rates for the more reactive olefins; bromine is used for the moderately reactive olefins; and chlorine is commonly used for the less reactive olefinic compounds. The relative rates are obtained from comparisons of rates within one set of data and between one set and another irrespective of the halogen used, provided that there is a compound common to both sets. It has been found[8] that the rate ratio for chlorine and bromine addition, under a given set of conditions is about 250 to 1 and is not critically affected by the structure and reactivity of the olefin. The relative rates for a given pair of compounds are about the same regardless of whether they are determined by chlorine or bromine addition.

The results of the study of relative rates of halo-

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[1] This is an abstract of a part of the doctoral thesis submitted by Lieng-Huang Lee, Present address: Dow Chemical Company, Midland, Mich.

[2] Part I, *J. Org. Chem.*, **23**, 1876 (1958); Part II, *J. Org. Chem.*, **24**, 1271 (1959).

[3] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931).

[4] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 984 (1935).

[5] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 1396 (1935).

[6] B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 630 (1947).

[7] P. W. Robertson, J. K. Heyes, and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952).

[8] P. B. D. De la Mare and P. W. Robertson, *J. Chem. Soc.*, 2838 (1950).