

tion of the transition state. In no case so far investigated does either mechanism alone completely satisfy both kinetic and isotopic tracer results.

The investigation of the decomposition of a series of substituted peroxybenzoic acids by Goodman, *et al.*⁶ is at present the most complete study of a group of structurally closely related acids and the data suggest that the contribution of decomposition by path I may not be inappreciable in this series. For this series of reactions there is no simple Hammett $\sigma\rho$ relationship between the logarithm of the rate constant and σ since substituents in the aromatic ring affect both substrate and nucleophile instead of only the substrate and also since the two mechanisms should have different ρ values. Indeed it was found⁶ that the decomposition rate constants exceeded that for peroxybenzoic acid whether electron-releasing or -attracting groups were substituted in the benzene ring.

The convenience and the usefulness of the double-labeling method for study of peroxide decompositions is exemplified well by the present investigation. Some other systems to which this technique is being applied

at present are the paramagnetic peroxyborates,¹³ the tetraperoxychromate ion,¹⁴ and peroxyipivalic acid.¹⁵ A combined kinetic and isotope study of the decompositions of substituted peroxybenzoic acids would give data of considerable value in understanding the factors which govern the reactivities of carbonyl carbon and peroxide oxygen to peroxyanions.

Acknowledgments. This work was supported in part by U. S. Air Force Grant AF-AFSOR-1027-66 and by the ARPA agency of the Defense Department. We thank the Leverhulme Trust Fund for a fellowship (to M. L. H.), Laporte Chemicals, Ltd., for financial assistance, the University of Newcastle upon Tyne for a leave of absence to Dr. Peter Jones, and Dr. G. O. Dudek of Harvard University for mass spectrometer facilities.

(13) K. Watters, private communication; *cf.* R. Bruce, J. O. Edwards, D. Griscom, R. A. Weeks, L. R. Darbee, W. DeKleine, and M. McCarthy, *J. Am. Chem. Soc.*, **87**, 2057 (1965).

(14) S. B. Brown, private communication; *cf.* D. Quane and J. E. Earley, *ibid.*, **87**, 3823 (1965).

(15) E. Koubek, private communication.

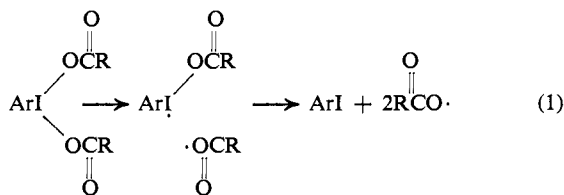
The Decomposition of Aryl Iodine Diacetates

J. E. Leffler and L. J. Story¹

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. Received December 2, 1966

Abstract: The decomposition of aryl iodine diacetates takes place by three mechanisms: nucleophilic displacement within an ion pair to give aryl acetate and iodine acetate (the major reaction), homolysis to aryl iodide and acetoxy radicals, and induced homolysis. The intermediate iodine acetate decomposes rapidly to carbon dioxide and methyl iodide, but may be trapped completely by cyclohexene. The radical chain homolysis of phenyl iodine diacetate is enhanced by di-*t*-butyl peroxide.

The decomposition of phenyl iodine dibenzoate² in aromatic solvents gives clear indications of the presence of phenyl radicals,^{3a,b,c} and it was at one time widely presumed to consist entirely of homolysis to benzyloxy radicals, in a process such as eq 1 or the corresponding single-step mechanism. However, a more detailed study of the products and kinetics re-



vealed a reaction of considerable complexity.^{3a} One of the products, in 8–25% yield, is phenyl benzoate. Labeling experiments established that the phenyl moiety of that ester comes exclusively from the aryl

iodine moiety of the dibenzoate and not at all from benzyloxy-derived phenyl radicals. This suggested that at least part of the reaction goes by way of an internal nucleophilic displacement (eq 2), closely analogous to a well-established major route for the decomposition of diaryliodonium compounds.⁴ Kinetic and other evidence indicated that the intermediate iodine benzoate interacted with additives such as benzoic anhydride or benzaldehyde to induce a radical chain decomposition of the dibenzoate, but the details of the mechanism remained conjectural. The behavior of the diacetate, as reported in the present paper, appears to be simpler and more amenable to mechanistic interpretation.

The Ion Pair Process. Table I and Figure 1 show the products and typical kinetic behavior of the decomposition of phenyl iodine diacetate in chlorobenzene under anhydrous conditions.⁵ The second yield col-

(1) Petroleum Research Foundation Predoctoral Fellow.

(2) The *Chemical Abstracts* name is (dihydroxyiodo)benzene diacetate.

(3) (a) J. E. Leffler, W. J. M. Mitchell, and B. C. Menon, *J. Org. Chem.*, **31**, 1153 (1966); (b) B. M. Lynch and K. H. Pausacker, *Australian J. Chem.*, **10**, 329 (1957); (c) D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1475 (1956).

(4) See, for example, F. M. Beringer and R. A. Falk, *ibid.*, 4442 (1964).

(5) Unless otherwise noted, the solvent is chlorobenzene containing 0.1 *M* acetic anhydride to reactylate any diacetate that may be hydrolyzed by traces of water. Within experimental error, the presence of this amount of acetic anhydride has no effect on the decomposition rate. Although the direct reaction between traces of water and acetic anhydride in chlorobenzene at 126.8° is very slow, the indirect reaction in the presence of phenyl iodine diacetate is extremely fast. Unless

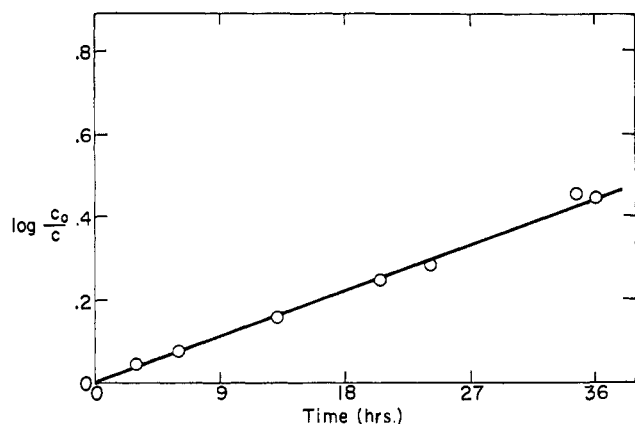


Figure 1. Typical phenyl iodine diacetate decomposition in chlorobenzene (0.1 *M* added acetic anhydride) at 126.8°. Initial concentration 0.02 *M*.

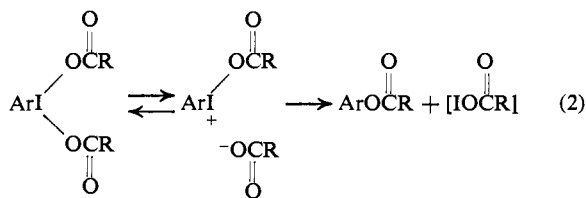
umn of Table I and the curves of Figure 2 show the effect of adding cyclohexene. The yield of methyl iodide is reduced drastically from 70 to 1% or less while the initial rate is left unchanged. The most plausible intermediate capable of giving methyl iodide in high

Table I. Products of Decomposition of Phenyl Iodine Diacetate in Chlorobenzene^a at 126.8°^b

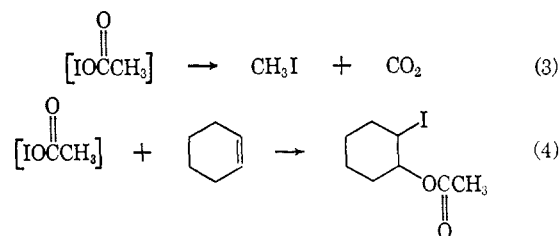
Product	Mole % per mole of diacetate	
	No cyclohexene	0.222 <i>M</i> cyclohexene
Methyl iodide	70.4	1
Iodobenzene	26.0	81.2
Phenyl acetate	74.6	20.0
Acetic acid	22.7	121.4
Chlorotoluenes ^c	10.8	2
Carbon dioxide	72.5	13.4
Methane	0	2
Benzene	0	22.3
2-Iodocyclohexyl acetate	...	≥7.7 ^e
<i>trans</i> -1,2-Diacetoxycyclohexane ^d	...	0.8

^a Containing 0.1 *M* acetic anhydride. ^b Product yields are ±3%. Results are the average of two experiments. Initial diacetate concentrations 0.0662 and 0.0732 *M* in the absence of cyclohexene, 0.0790 and 0.0765 *M* in the presence of cyclohexene. ^c 63% *ortho*, 24% *meta*, and 13% *para*. ^d 0.08 mole % of the *cis* isomer also believed to be present. See Experimental Section. ^e 2-Iodocyclohexyl acetate partly decomposes during vapor chromatography.

yield yet capable of reacting still more rapidly with cyclohexene is undoubtedly iodine acetate. The expected diversion product, 2-iodocyclohexyl acetate, is indeed isolated, although in low yield. Reactions 2 and 3 account for 70–75% of the decomposition in the absence of cyclohexene.



water is carefully excluded or removed in this way the rates are not reproducible.



Iodine acetate has never been isolated, but has been postulated as an intermediate in the Hunsdiecker and Simonini reactions, the reaction of lead tetraacetate, iodine, and carboxylic acids,^{6,7} the reaction of iodine and peracetic acid with cyclohexene⁸ or with aromatic compounds,⁹ in the decomposition of iodine triacetate,¹⁰ and the decomposition of acetyl peroxide in chlorobenzene in the presence of iodine.¹¹

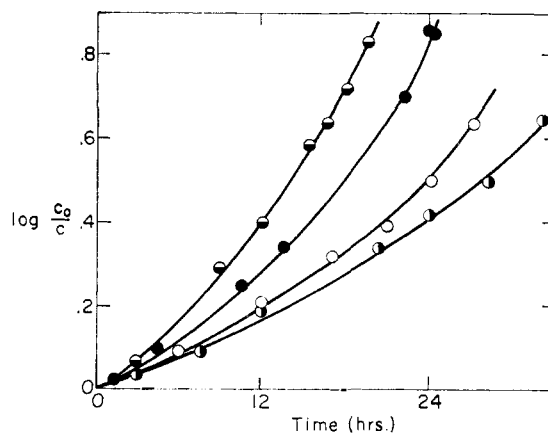


Figure 2. Effect of varying cyclohexene concentration on the rate of decomposition of 0.034 *M* phenyl iodine diacetate in chlorobenzene at 126.8°: ●, 0.181 *M* cyclohexene; ●, 0.0678 *M*; ○, 0.0271 *M*; ○, 0.013 *M*.

The decomposition of phenyl iodine diacetate in the presence of cyclohexene is complicated in its later stages by a secondary reaction between phenyl iodine diacetate and 2-iodocyclohexyl acetate. This reaction accelerates the decomposition of the diacetate as 2-iodocyclohexyl acetate accumulates in the latter part of each run, and increases the yield of iodobenzene and acetic acid at the expense of phenyl acetate. Experiments in which 2-iodocyclohexyl acetate was added initially gave a very fast decomposition of the phenyl iodine diacetate from the beginning of the reaction. These rates were not readily reproducible, however, and in view of the instability of 2-iodocyclohexyl acetate and the difficulty in obtaining pure samples of known stereochemical composition the reaction was not investigated further. Judging from the yield data in Table I, the accelerated part of the decomposition in the presence of cyclohexene gives iodobenzene, acetic acid, and benzene as the major products. Since

(6) D. H. R. Barton, H. P. Faro, E. P. Serebrayakov, and N. F. Woolsey, *J. Chem. Soc.*, 2438 (1965).

(7) G. B. Bachman and J. W. Wittman, *J. Org. Chem.*, 28, 65 (1963).

(8) Y. Ogata, K. Aoki, and Y. Furuya, *Chem. Ind. (London)*, 304 (1965).

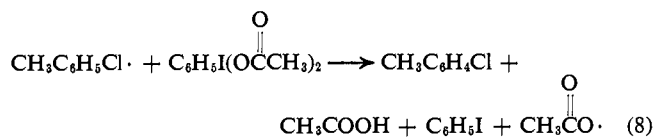
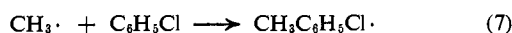
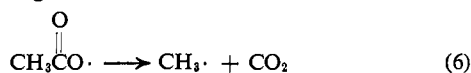
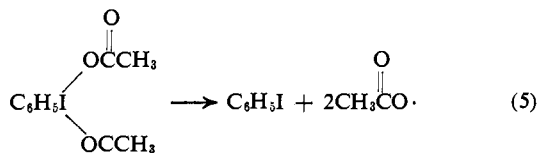
(9) Y. Ogata and K. Nakajima, *Tetrahedron*, 20, 2751 (1964).

(10) J. W. H. Oldham and A. R. Ubbelohde, *J. Chem. Soc.*, 368 (1941).

(11) G. S. Hammond and G. Moses, private communication.

the original phenyl groups are otherwise accounted for, the 22.3 mole % of benzene probably comes from the cyclohexene. A direct chain transfer between acetoxy radicals and cyclohexene to give radicals responsible for the induced decomposition of the phenyl iodine diacetate is unlikely in view of the slowness of the initial decomposition. A similar chain transfer between acetoxy radicals and 2-iodocyclohexyl acetate, however, would fit the delayed acceleration produced by added cyclohexene, the immediate acceleration produced by added 2-iodocyclohexyl acetate, and also the formation of benzene and acetic acid. We envisage a process in which the attacking radical, derived from 2-iodocyclohexyl acetate, supplies a hydrogen atom and induces the decomposition of the phenyl iodine diacetate into a molecule of acetic acid, a molecule of iodobenzene, and a new chain-carrying acetoxy radical. The dehydrogenated radical could then react further to give benzene by disproportionation, elimination, or further donation of hydrogen to phenyl iodine diacetate or to acetoxy radicals.

The Free-Radical Reaction. The other products shown in Table I, phenyl iodide, isomeric chlorotoluenes, and acetic acid, could be assigned to homolytic reactions such as eq 5–8. The presence of free



radicals is indicated by the initiation of acrylonitrile polymerization, the presence of methyl radicals in particular by the chlorotoluene isomer ratios which are very close to those observed when di-*t*-butyl peroxide¹² or methylmercuric iodide¹³ is used as the radical source.

Homolysis of phenyl iodine diacetate to give two acetoxy radicals (eq 5) is superficially like the first step in the homolysis of acetyl peroxide,¹⁴ but the higher temperature required and the greater initial distance between the acetoxy radicals should greatly reduce the amount of geminate recombination. The total absence of ethane and methyl acetate is, therefore, in no way remarkable and does not necessarily mean that the two acetoxy radicals are formed in separate steps.

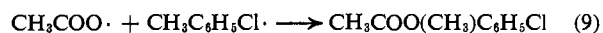
Radical-Induced Decomposition. The substantial amount of acetic acid formed in the decomposition of phenyl iodine diacetate is very unlikely to come from

(12) B. R. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).

(13) G. H. Williams and G. E. Corbett, *Proc. Chem. Soc.*, 240 (1961); *J. Chem. Soc.*, 3437 (1964).

(14) (a) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966); (b) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961); (c) T. W. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965); (d) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5981 (1954).

reaction of acetoxy radicals with the solvent. In the decomposition of acetyl peroxide in isooctane, no more than 1% of the acetoxy radicals react in that way.^{14d} Alternative explanations for the acetic acid are induced decomposition *via* eq 8,¹⁵ eq 9–10, or eq 11. Induced



decomposition according to the sequence 5–8 with either 9–10 or 11 as the chain-breaking steps would give a first-order and kinetically undetectable contribution to the rate law. The first-order rate constants in Table II do not appear to be very sensitive to the initial concentration of phenyl iodine diacetate, but since the total participation of homolytic processes is only 25%, a small contribution from reactions of other than first order could easily escape detection.

Table II. Effect of Initial Concentration of Phenyl Iodine Diacetate on Rate in Chlorobenzene^a at 126.8°

$10^3 \times C_0, M$	$10^6 \times k, \text{sec}^{-1}$	$10^3 \times C_0, M$	$10^6 \times k, \text{sec}^{-1}$
3.05	7.16	25.76	7.46
7.39	7.38	36.44	6.67
16.72	7.70	45.31	6.61
20.96	7.68	23.02	7.57 ^b

^a With 0.1 *M* acetic anhydride. With less acetic anhydride the rates are not reproducible unless elaborate precautions are taken to ensure dryness. Runs in ordinary solvent without added anhydride start with a very high rate constant, decreasing later in the run to that obtained in the presence of anhydride. The initial fast reaction is also suppressed by added acetic acid. The rate constant is the same as that for the reaction in the presence of acetic anhydride.

^b With 0.2 *M* acetic anhydride.

The potential chain inhibitors, trinitrobenzene and iodine, appeared to accelerate the decomposition slightly,¹⁶ though only by 15% or less. Styrene, like cyclohexene, caused an increased rate late in the run but had no effect on the initial rate. Diethyl ether (0.14 *M*) had no effect. *On the other hand the addition of di-*t*-butyl peroxide as an independent source of methyl radicals gave a pronounced acceleration* (Figure 3).

Benzoic anhydride in chlorobenzene causes an accelerated first-order decomposition of phenyl iodine diacetate after a short delay during which the reaction apparently proceeds at about its normal rate (Figure 4). This behavior is very much like the effect of benzoic anhydride on the decomposition of phenyl iodine dibenzoate^{3a} except that the final value of the rate constant is $19.0 \times 10^{-6} \text{ sec}^{-1}$ instead of the $61 \times 10^{-6} \text{ sec}^{-1}$ obtained in the case of the dibenzoate. In the latter investigation it was demonstrated that benzoic anhydride trapped some intermediate quantitatively, eventually producing a critical concentration of a chain-transfer agent responsible for the accelerated reaction. A possible explanation for the acceleration of the decomposition of the diacetate by benzoic anhydride is

(15) A similar explanation has been suggested by Lorand for the formation of acetic acid (23 mole %) in the decomposition of *t*-butyl peracetate in chlorobenzene at 140°: J. P. Lorand, Dissertation, Harvard University, 1964.

(16) Aromatic nitro compounds accelerate the decomposition of benzoyl peroxide: B. B. Gill and G. H. Williams, *J. Chem. Soc., Phys. Org.*, 880 (1966).

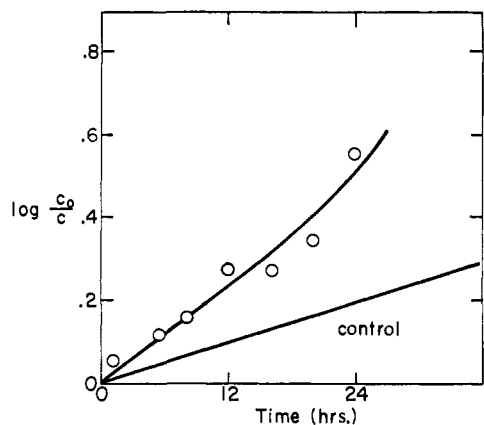


Figure 3. Effect of added di-*t*-butyl peroxide ($3.55 \times 10^{-3} M$) on the rate of decomposition of phenyl iodine diacetate ($21.9 \times 10^{-3} M$) in chlorobenzene at 126.8° .

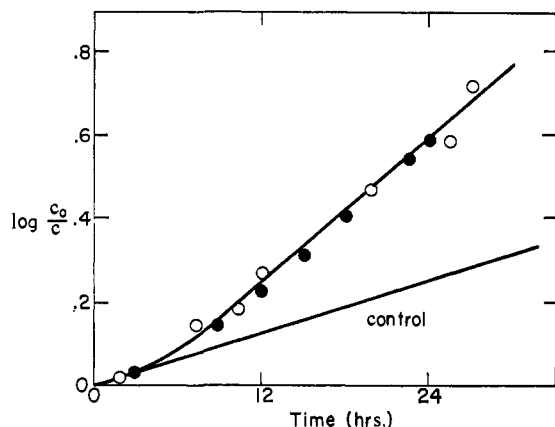


Figure 4. Effect of added benzoic anhydride on the rate of decomposition of phenyl iodine diacetate at 126.8° : ●, C_0 0.0241 *M*, benzoic anhydride 0.050 *M*, ordinary solvent; ○, C_0 0.0216 *M*, benzoic anhydride 0.070 *M*, very carefully dried solvent.

again the trapping of some intermediate, presumably iodine acetate, with the formation of a slightly different chain-transfer agent. However, exchange of acetate and benzoate groups cannot be ruled out.¹⁷

Another probable instance of induced decomposition is the rapid reaction at room temperature between the diacetate and cyclohexene in undegassed chlorobenzene solutions. This reaction takes place with or without acetic anhydride, and loss of oxidizing titer is complete within 48 hr. Phenyl acetate is no longer detectable, and the major products are acetic acid, iodobenzene (100%), 2-cyclohexen-1-one (42% based on the phenyl iodine diacetate), 2-cyclohexen-1-ol (16%), and cyclohexene oxide (3.6%).¹⁸

Substituent Effects. Table III shows the effects of *meta* and *para* substituents on the rate of decomposition of phenyl iodine diacetate at two temperatures. Log k is correlated with σ , the ρ value being about 0.8 at 126.8° ,

(17) A reverse experiment by W. J. Mitchell (this laboratory) in which a 0.005 *M* solution of phenyl iodine dibenzoate was decomposed in the presence of 0.01 *M* acetic anhydride in chlorobenzene at 126.8° gave an initial fast reaction consuming about 10% of the oxidizing titer, then a first-order rate constant of $13 \times 10^{-6} \text{ sec}^{-1}$. The reaction was followed to 50% completion, well past the usual time for acceleration in an ordinary run using phenyl iodine dibenzoate in the presence of 0.01 *M* benzoic anhydride.

(18) These yields are from an experiment with 0.125 *M* phenyl iodine diacetate and 4.88 *M* cyclohexene in benzene as solvent to facilitate separation of the cyclohexene oxide.

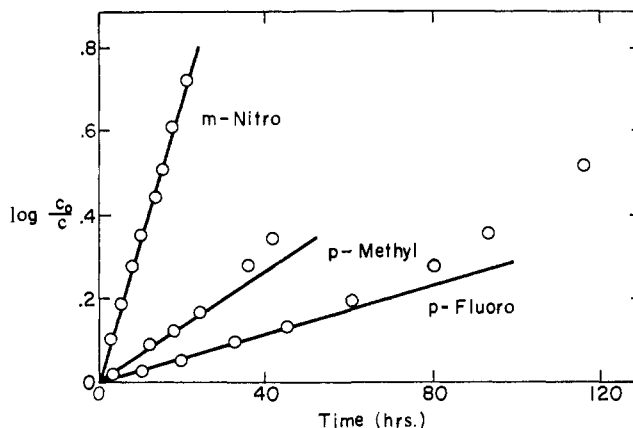


Figure 5. Decomposition of three aryl iodine diacetates illustrating curvature of first-order rate plots when electron-releasing substituents are present.

but even this rather rough correlation requires the exclusion of *para* substituents capable of strong resonance interactions, whether electron donating or electron withdrawing. Neglecting the contribution from the homolytic part of the reaction for the moment, the observed first-order rate constants should be functions of k_1 and k_{-1} , rate constants for the ionization and recombination steps of eq 1, and k_2 , the rate constant

Table III. Rate Constants^a for the Decomposition of Substituted Phenyl Iodine Diacetates in Chlorobenzene^{b,c}

Substituent	$10^6 \times k, \text{ sec}^{-1}$	
	126.8°	150.1°
<i>p</i> -Methoxy	1.59	13.6
<i>p</i> -Fluoro	1.78	
<i>p</i> -Methyl	4.20	30.5
<i>p</i> -Phenyl	4.35	52.5
Hydrogen ^d	7.24 ^d	60.9
<i>m</i> -Chloro	10.5	106
<i>p</i> -Chloro	6.19	49.5
<i>m</i> -Nitro	21.1	201
<i>p</i> -Carbomethoxy	42.3	389

^a In view of the complexity of the reaction, the activation parameters are of no theoretical significance. ^b The solvent contained acetic anhydride, 0.1 *M*. ^c Initial concentrations were usually in the range 0.02–0.03 *M*. ^d Mean of seven runs in Table II.

for the nucleophilic displacement step. Since the iodine-oxygen bonds in the diacetate are already quite

$$k_{\text{obsd}} = k_1 k_2 / (k_2 + k_{-1}) \quad (12)$$

polar, only a small negative value of ρ is expected for the ionization equilibrium. The net effect should be dominated by the positive ρ of the nucleophilic displacement.¹⁹ A further source of complexity in the substituent effects is variation in the relative rate of the homolytic part of the reaction. As can be seen in Figure 5, runs in which the substituent is electron releasing show a distinct increase in first-order rate constant in the latter part of the reaction.²⁰ The electron-releasing substituents may not decelerate the homolytic reaction,

(19) A different relative importance of inductive and resonance effects in the two steps would seriously perturb any simple free-energy relationship involving k_{obsd} : J. E. Leffer and E. Grunwald "Rates and Equilibria of Organic Reactions," Interscience Publishers, Inc., New York, N. Y., 1963.

(20) In such cases the tabulated rate constants are initial values.

particularly the induced part, to the same extent as the ion-pair reaction. If the homolytic reaction gives rise to any cyclohexadienes,²¹ their reaction with iodine acetate should give an efficient chain-transfer agent comparable to 2-iodocyclohexyl acetate. Whatever the explanation for the autocatalysis, the products from the *p*-fluoro derivative clearly indicate a decreased relative rate for the ion-pair part of the reaction. The yields per mole of diacetate were as follows: methyl iodide, 37.4%; acetic acid, 27.6%; *p*-fluoroiodobenzene, 54.1%; and *p*-fluorophenyl acetate, 48.0%.

Experimental Section

Chlorobenzene was stirred with three portions of sulfuric acid and washed with water and sodium bicarbonate solution. After successive 24-hr periods of drying with CaCl₂, anhydrous CaSO₄, and P₂O₅, it was distilled from P₂O₅ through a 35-in. column packed with 0.25-in. glass helices. A middle fraction, bp 131.1–132.1°, was collected.

Acetic anhydride was distilled through the glass helices column. After a large forerun, a middle fraction, bp 139.0°, was collected.

Cyclohexene (bp 83.1–83.5°) was refluxed over Na in a nitrogen atmosphere. Samples were taken off as needed by distillation through a 1-ft glass helices column. Cyclohexene exposed to the air for 2 days gave a positive peroxide test.

Benzoic anhydride (mp 40.0–41.5°) was twice recrystallized from benzene and petroleum ether (bp 60–70°). It was shown by infrared spectroscopy to be free from benzoic acid.

Aryl Iodine Diacetates. The substituted phenyl iodine diacetates were prepared by a procedure like that given for *m*-chlorophenyl iodine diacetate (see Table IV for melting point data).

Table IV

Subst	Mp, °C	Subst	Mp, °C
<i>p</i> -Fa, ^b	177.0–179.8 ^d	<i>m</i> -NO ₂ ^{f,g}	151.0–154.2 ^d
<i>p</i> -COOCH ₃ ^{a,c}	150.0–153.3 ^d	<i>p</i> -C ₆ H ₅ ^h	141.0–144.1
<i>o</i> -OCH ₃ ^a	146.9–150.1	<i>p</i> -Cl ^{d,i}	109.8–113.2 ^d
<i>p</i> -CH ₃ ^{d,e}	106–110 ^d	<i>m</i> -Cl ^{f,i}	153.1–154.7 ^d
<i>p</i> -CH ₃ O ^f	92.4–96.0	H ^k	161.1–162.2 ^d

^a This paper. ^b Oxidizing titer 99 and 99.5% of theoretical. The bis(trideuterioacetate) melts at 183.7–185.8°. It exchanges carboxylate groups rapidly with acetic acid solvent. ^c Oxidizing titer 102 and 102% of theoretical. ^d K. H. Pausacker, *J. Chem. Soc.*, 107 (1953). ^e Lit.^d gives 107°. ^f C. H. C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigem Jod," F. Enke, Stuttgart, 1914. ^g Lit.^f gives 155°. ^h Lit.^f gives 140°. J. G. Sharefkin and H. Saltzman, *Anal. Chem.*, **35**, 1428 (1963). ⁱ Lit.^d gives 104°. ^j Lit.^f gives 155°. ^k Lit. gives 158°. I. Lillien, *J. Chem. Soc.*, 4498 (1962).

***m*-Chlorophenyl Iodine Diacetate.** To 23.8 g (0.1 mole) of *m*-chloroiodobenzene was added dropwise with stirring 31 ml (0.24 mole) of 40% peracetic acid. The flask was chilled with an ice-water bath during the slow addition (1 hr). Two phases separated, but on continued stirring the solution became homogeneous. The solution was stirred for an additional hour at 20–25° and then cooled in an ice-salt bath. The white crystals which formed were washed quickly with ice-cold water. (Warm water may cause hydrolysis of the diacetate to the aryl iodine oxide, particularly in the case of the *p*-methoxy-substituted compound.) The crystals were pressed dry and dried overnight *in vacuo* over P₂O₅. (The use of CaCl₂ instead of P₂O₅ caused the crystals to turn yellow.) Recrystallization was effected from a minimum amount (1.5 ml/g) of 1:4 acetic anhydride-acetic acid, yield, 22.5 g (63%); mp 154.5–156.5° (lit.²² 154°). Pure dry benzene (10 ml/g) could also be used for the recrystallization.

Kinetic Procedure. At no time was the purity of the aryl iodine esters used in the kinetic runs less than 98.5%. Standard solutions

in chlorobenzene were checked by iodometric titration before a run was started.

Kinetic runs were made in 18 × 150 mm test tubes fitted with a standard taper, ground glass joint. The tubes were cleaned with hot chromic acid cleaning solution and rinsed repeatedly with water, dilute ammonium hydroxide, water, and distilled water. The tubes were oven dried and a constriction was added for sealing. Before use, the tubes were fitted to a vacuum system and leak tested with a Tesla coil.

The tubes were flushed with prepurified²³ nitrogen, and aliquots of the diacetate solution were added to each tube from a calibrated pipet. Each tube was then attached to the vacuum system and put through a four-cycle freeze-degas-thaw procedure. The final pressure in the vacuum system was less than 0.005 mm. The tubes were sealed and removed for use or storage at 5°. Kinetic runs using tubes degassed fewer than three times were usually not reproducible.

For the experiments with "carefully dried solvent" aliquots of diacetate solutions were pipetted into standard constricted tubes. These tubes and unconstricted tubes containing phosphorus pentoxide were attached to the vacuum line. The chlorobenzene was degassed three times, distilled into the phosphorus pentoxide tube, allowed to stand for 1 hr at room temperature, and redistilled into the original tube. After one more degassing cycle, the tube was sealed. For experiments with cyclohexene, the constricted tubes were fitted with a rubber serum cap and the cyclohexene was injected with a syringe just before the last degassing cycle.

Normally, eight tubes were used in each kinetic run. Since the half-life for the decomposition of phenyl iodine diacetate at 126.8° in chlorobenzene is about 24 hr, the warm-up period for the tubes is insignificant and the zero point was determined from an aliquot of the prepared solution. This also provided a constant check on diacetate purity.

For short runs (*ca.* 6 hr or less), all tubes were placed in the bath and the zero-point tube was removed when the temperature of the bath returned to equilibrium. An accurate account of the temperature was kept by a thermistor-Wheatstone bridge-recorder arrangement.²⁴ During the shorter runs, tubes were quenched in ice water.

For analysis the contents of the tubes were decanted and rinsed out with two 1-ml portions of pure chlorobenzene. The concentration of diacetate was determined by iodometric titration:²⁵ (1) add 10 ml of fresh acetic acid (acetic acid left exposed to the air gives high blank values), (2) add pellets of carbon dioxide to the flask and at the same time to 25 ml of distilled water, (3) prepare a fresh solution of saturated potassium iodide and add 3 ml to the flask, (4) swirl the flask and add the deaerated water, (5) titrate immediately to a starch-iodine end point with approximately 0.015 to 0.10 *N* sodium thiosulfate using a magnetic stirrer for mixing. This titration occurs in a two-phase system; however, excellent results have been obtained with both benzene and chlorobenzene solutions of the diacetate. The use of acetic acid as a solvent for iodometric titrations has been criticized²⁶ but titrations of benzene solutions of freshly recrystallized benzoyl peroxide showed purities greater than 99%.

Product Analysis. Phenyl iodine diacetate was weighed into a modified Pyrex hydrogenation bomb (A) and the constriction rinsed clean with a few milliliters of chlorobenzene. Approximately 300 ml of purified chlorobenzene was added to a second bomb (B) along with several grams of phosphorus pentoxide and a magnetic stirring bar. The entire apparatus was attached to a vacuum system and bomb B was degassed using a three-cycle freeze-degas-thaw procedure. The solution was stirred for 1 hr at room temperature at the end of the third cycle. Bomb A was then cooled with liquid nitrogen and the chlorobenzene in bomb B allowed to distil into bomb A. Stirring was continued to prevent bumping. After all the liquid had been distilled, the system was degassed twice more and the constriction sealed with a flame. The bomb was then placed in the thermostated bath.

After about ten half-lives, the bombs were removed, cooled, wiped clean, and attached to the vacuum system. After the system was evacuated, the capillary tip was broken, and the gases were allowed to distil into the liquid nitrogen trap. The bomb was re-

(23) Minimum purity: 99.997%; dew point: -85°F, contains 8 ppm oxygen.

(24) This apparatus was designed and built by Mr. Vern Champeaux.

(21) See, for example, the decomposition of benzoyl peroxide in aromatic solvents: D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

(22) A. R. Fox and K. H. Pausacker, *J. Chem. Soc.*, 295 (1957).

(25) J. P. Wibaut, H. B. vanLeeuwen, and B. van der Waal, *Rec. Trav. Chim.*, **73**, 1033 (1954).

(26) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

frozen with Dry Ice-isopropyl alcohol and the pressure of the non-condensable gases recorded. The liquid nitrogen bath was removed and the total gas pressure recorded.

The gases were thoroughly mixed using a Toepler pump and then forced by external pressure into a gas sampler fitted with a rubber serum cap. A gas-tight Hamilton syringe was used to transfer the gas mixture to a F & M Model 700 gas chromatograph with a thermal conductivity detector.²⁷ Air, methane, ethane, and carbon dioxide are easily resolvable and a check was made of their separation before an unknown was measured.

After the sample had been removed, the system was evacuated and the bomb degassed a second time. The pressure was measured and added to the first pressure reading. The system was reevacuated and the total volume calculated by admitting a known volume of gas at atmospheric pressure and observing the final pressure.

The Dry Ice-isopropyl alcohol trap was rinsed with chlorobenzene and the washings were added to the main solution. For qualitative identification the solution was distilled and three fractions were collected; a 5-ml forerun, bp 25–130°; ca. 300 ml of chlorobenzene, bp 130°; and a high boiling residue (ca. 20 ml). Each of the fractions was subjected to gas chromatography (10 ft × 0.25 in. SF-96 silicone oil, 7 ft × 0.25 in. DEGS,²⁸ 7 ft × 0.25 in. PPE,²⁹ and 7 ft × 0.25 in. FFAP³⁰ columns). Peaks were collected

(27) Conditions: 12 ft × 0.25 in. copper column; 30–60 mesh silica gel; oven, 70–90°; detector, 80°; injector, 52°; helium, 37 cc/min; sample, approximately 30 μ l.

(28) Diethylene glycol succinate.

(29) Polyphenyl ether.

(30) A specially modified Carbowax obtained from Wilkins Instrument and Research Corp., Walnut Creek, Calif.

and identified by comparing their infrared and nmr spectra and gas retention times with those of authentic samples.

Quantitative measurements were performed using standard solutions of known compounds. Each peak was bracketed by injecting enough of the standard solutions so that both a smaller and a larger peak than that of the unknown compound was obtained. Analyses were made using the same chromatographic conditions. All analyses were made in duplicate.

No low-boiling compounds other than methyl iodide were observed. Methyl acetate was found to be completely resolved from methyl iodide at 35° using a 7 ft × 0.25 in. DEGS column; it was not present in the product mixture.

No high-boiling compounds other than those mentioned were detected. Biphenyl, phenol, *o*- and *m*-iodochlorobenzene, *o*-iodophenyl benzoate, *p*-chlorobenzyl acetate, and *p*-chlorophenyl acetate were shown to be absent (or if present, in less than 1% yield) by control experiments.

Determination of Chlorotoluene Isomer Ratios. The chlorotoluene isomer ratios were determined by gas chromatography, using the liquid crystal technique recently developed by Dewar and Schroeder³¹ and an F & M Model 700 flame ionization chromatograph at 125°. Peak height-to-composition conversion factors were determined experimentally for each isomer.

Acknowledgments. We are happy to acknowledge support of this research by the Petroleum Research Foundation and by the National Science Foundation.

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Decarbonylation of Aromatic Carbonyl Compounds Catalyzed by Rhodium Complexes

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Received December 29, 1966

Abstract: The catalytic decarbonylation of aroyl chlorides, bromides, and cyanides with chlorotris(triphenylphosphine)rhodium(I) has been investigated; particular attention has been paid to polycyclic aroyl halides. A theory of the mechanism of decarbonylation has been suggested which accounts for the observations made in this study. The essential features of the theory are the formation of V, its isomerization to VI, and the loss of carbon monoxide from the latter. Several new rhodium complexes are described.

A previous communication from this laboratory² reported that chlorotris(triphenylphosphine)rhodium(I) catalyzes the decarbonylation of aroyl chlorides to the corresponding aryl chlorides. Almost simultaneously, Tsuji and Ohno observed that aliphatic acyl chlorides are converted, under the same conditions, into olefins.³ In both cases, the analogous response of acyl bromides was briefly mentioned.^{3,4}

The Japanese authors suggested a mechanism for these decarbonylation reactions. This mechanism will have to be somewhat modified in view of the more extensive studies reported in the present paper.

In Table I, the results obtained with a number of benzoyl chlorides are summarized. This table also

contains some examples for the decarbonylation of benzoyl and naphthoyl bromides. The last two examples in this table indicate that carbon monoxide can be extruded also from benzylic carbonyl chlorides without difficulty.^{2,3} It is obvious from these data that the reaction is practically unaffected by electronic or steric influences of substituents; the seemingly accelerating effect of the α -naphthoyl residue (compare benzoyl and α -naphthoyl bromide) is most probably due to the higher temperature at which the reaction with α -naphthoyl bromide is carried out.

The behavior of the three isomeric phthaloyl chlorides deserves some comment. *o*-Phthaloyl chloride does not react at all, possibly because it has the structure of α,α -dichlorophthalide.⁵ The other two isomers decompose in two distinct steps, *via* the chlorobenzoyl chlorides, into the dichlorobenzenes. This is in

(1) To whom inquiries should be addressed at the Department of Organic Chemistry, Hebrew University, Jerusalem.

(2) J. Blum, *Tetrahedron Letters*, 1605 (1966).

(3) J. Tsuji and K. Ohno, *ibid.*, 4713 (1966).

(4) Cf. J. Blum, *ibid.*, 3041 (1966).

(5) F. B. Garner and S. Sugden, *J. Chem. Soc.*, 2877 (1927).