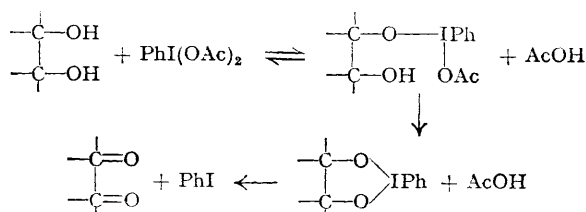


18. The Oxidation of Glycols by Aryl Iodosoacetates. A Kinetic Study.

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The rates of oxidation of *isohydrobenzoin* by aryl iodosoacetates in acetic acid have been measured. The results obtained were in accord with the general conclusions made on glycol oxidation in the previous paper.

CRIGEE and BEUCKER (*Annalen*, 1939, **541**, 218) investigated the reactions of compounds of the type $\text{RI}(\text{O}\cdot\text{COR}')_2$ (where R = aryl; R' = alkyl or aryl) and found that they resemble lead tetra-acetate in their general reactions. These authors paid particular attention to the formation of glycol diacetates from olefins, and the oxidation of glycols forming carbonyl compounds. Their mechanism for the oxidation of glycols is similar to that proposed by Criegee for lead tetra-acetate oxidation (see preceding paper) as shown below :



The present work is concerned with the oxidation of *isohydrobenzoin* by aryl iodosoacetates in acetic acid solution.

EXPERIMENTAL

Preparation of Aryl Iodosoacetates.—Willgerodt's general method (*J. pr. Chem.*, 1886, **33**, 156; 1899, **59**, 198) was used, the aryl iodide being converted into the iododichloride which is hydrolysed to the iodoso-compound, treatment of which with acetic acid yields the iodosoacetate. The following substituted phenyl iodosoacetates were prepared.

Substituent	M. p.		Equiv. :		Substituent	M. p.		Equiv. :	
	Found	Lit.	Found	Calc.		Found	Lit.	Found	Calc.
—	158°	158°	161	161	<i>p</i> -Cl *	104°	—	179	178
<i>p</i> -Me *	104	—	166	168	<i>m</i> -Cl	154	155°	176	178
<i>m</i> -Me	154	148	166	168	<i>m</i> -NO ₂	155	155	183	183.5

* New compounds.

Phenyl iodosoacetate is best prepared by a modification of the method suggested by Böseken and Schneider (*ibid.*, 1931, **131**, 285). Hydrogen peroxide (30%, 70 ml.) and acetic anhydride (305 ml.) were stirred together for 4 hours at 40°. Iodobenzene (50 g.) was added to the solution, which was then kept overnight. Some phenyl iodosoacetate crystallised and was filtered off; the filtrate was concentrated to a small volume under reduced pressure (70 mm.), and a second crop obtained. The combined crystals were washed with ether and dried (NaOH) in a vacuum desiccator (yield 52 g.; m. p. 158°).

Acetic acid was purified as described in the preceding paper.

isoHydrobenzoin was prepared by catalytic reduction of benzoin (Buck and Jenkins, *J. Amer. Chem. Soc.*, 1929, **51**, 2163), m. p. 134°.

Apparatus and Method of Estimation.—A bath was used whose temperature was controlled within $\pm 0.05^\circ$. *isoHydrobenzoin* (0.16—0.20 g.) was accurately weighed into a 50-ml. standard flask. When the flask had attained the temperature of the bath, a 0.02M-acetic acid solution of the aryl iodosoacetate, previously heated to the temperature of the bath, was added to make up to the mark. When the *isohydrobenzoin* had dissolved, 5-ml. aliquots were withdrawn at determined times and added to acidified potassium iodide solution. The liberated iodine was titrated with 0.02N-sodium thiosulphate solution (starch). The initial aryl iodoso-

acetate solution was estimated in the same way. All experiments were run in duplicate, and agreement was generally within 5%.

Results.—The reaction of phenyl iodosoacetate with *isohydrobenzoin* at 45.4° has been chosen as a typical example.

Wt. of *isohydrobenzoin* = 0.1757 g. (\equiv 8.12 ml. 0.02018N- $\text{Na}_2\text{S}_2\text{O}_3$).

Initial phenyl iodosoacetate titre = 9.84 ml.

First phenyl iodosoacetate estimation = 8.40 ml. (a).

Equivalent *isohydrobenzoin* concn. = 6.68 ml. (b).

Time (min.)	25	50	75	100	125	150	200
Titre {	obs.	7.35	6.56	5.97	5.45	5.02	4.67
	calc.	7.38	6.55	5.91	5.39	5.06	4.72

By the method given in the preceding paper (p. 104), it was found that $k = 7.28 \times 10^{-3}$ mole $^{-1}$ l. sec. $^{-1}$.

The results obtained at different temperatures are summarised herewith, means being given in parentheses :

Temp.	24.8°	34.7°	45.4°
10 ³ k	0.692, 0.660 (0.676)	2.14, 2.09 (2.12)	7.28, 6.70 (6.99)

The bimolecular constants obey the Arrhenius equation as shown by the following data, where the calculated values are given by $k = 3.39 \times 10^{12} e^{-21,330/RT}$:

Temp.	24.8°	34.7°	45.4°
10 ³ k {	obs.	0.676	2.12
	calc.	0.692	2.14

The results obtained with different phenyl iodosoacetates and *isohydrobenzoin* in acetic acid are summarised below :

Substi- tuent	T	k × 10 ³	10 ⁻¹³ A	E (kcal.)	Substi- tuent	T	k × 10 ³	10 ⁻¹³ A	E (kcal.)
<i>p</i> -Me	34.7°	1.57, 1.61	36.3	21.6	<i>p</i> -Cl	24.9°	1.84, 1.69	1.48	21.6
	45.4	5.16, 5.28				30.5	3.57, 3.55		
	52.8	11.3, 11.4				34.7	5.56, 5.52		
<i>m</i> -Me	34.7	1.77, 1.86	26.3	21.3	<i>m</i> -Cl	24.5	2.63, 2.63	4.17	22.0
	45.6	5.40, 5.71				29.9	5.20, 5.03		
	52.9	12.5, 13.0				34.7	9.11, 8.99		
—	24.8	0.692, 0.660	33.9	21.3	<i>m</i> -NO ₂	25.1	8.61, 8.46	93.3	20.5
	34.7	2.14, 2.09				30.0	13.3, 13.0		
	45.4	7.15, 6.64				34.7	24.5, 25.5		

DISCUSSION

It is seen that the six compounds investigated have *A* and *E* values which are very close to each other as may, perhaps, be expected with the interaction of such large molecules. However, when the *k* values at 34.7° are compared, it is found that electron-repelling groups decrease the rate of reaction and electron-attracting groups have the opposite effect. Furthermore, it is found that a good linear plot is obtained when Hammett's equation is applied.

This is in accord with the type of mechanism proposed for lead tetra-acetate in the preceding paper, *viz.*,



It is thus seen that if electron-attracting groups are present in the aryl group, then the equilibrium in stage 1 will lie further to the right with a consequent increase in rate.

We have also found (unpublished results) that phenyl iodosoacetate converts many primary aromatic amines into the corresponding azobenzenes, in agreement with Neu (*Ber.*, 1939, 72, 1507) who found that azobenzene can be prepared from aniline and phenyl

