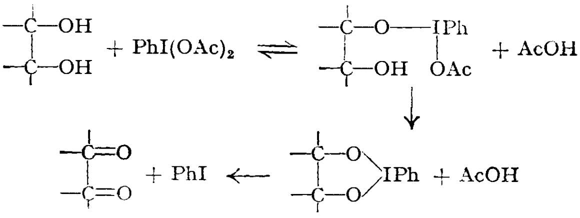
18. *The Oxidation of Glycols by Aryl Iodosoacetates. A Kinetic Study.*

By K. H. Pausacker.

The rates of oxidation of *iso*hydrobenzoin 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.

Criegee and Beucker (*Annalen,* **1939**, **541**, 218) investigated the reactions of compounds of the type $RI(O \cdot COR')_2$ (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 *iso*hydrobenzoin 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.

	M. p.		Equiv.:			M. p.		Equiv.:	
Substituent	Found	Lit.	Found	Calc.	Substituent	Found	Lit.	Found	Calc.
—	158°	158°	161	161	*p*-Cl *	104°	—	179	178
p-Me *	104	—	166	168	*m*-Cl	154	155°	176	178
m-Me	154	148	166	168	*m*-NO_2	155	155	183	183·5

* New compounds.

Phenyl iodosoacetate is best prepared by a modification of the method suggested by Böeseken 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.

*iso*Hydrobenzoin 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 ±0·05°. *iso*Hydrobenzoin (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 *iso*hydrobenzoin 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 iodosoacetate 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 *iso*hydrobenzoin af 45·4° has been chosen as a typical example.

Wt. of *iso*hydrobenzoin = 0·1757 g. (≡ 8·12 ml. 0·02018N-$Na_2S_2O_3$).
Initial phenyl iodosoacetate titre = 9·84 ml.
First phenyl iodosoacetate estimation = 8·40 ml. (*a*).
Equivalent *iso*hydrobenzoin 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	4·17
Titre calc.	7·38	6·55	5·91	5·39	5·06	4·72	4·14

By the method given in the preceding paper (p. 104), it was found that $k = 7{\cdot}28 \times 10^{-3}$ 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°
10^3k	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 $k = 3{\cdot}39 \times 10^{12}e^{-21{,}330/RT}$:

Temp.	24·8°	34·7°	45·4°
10^3k obs.	0·676	2·12	6·99
10^3k calc.	0·692	2·14	7·08

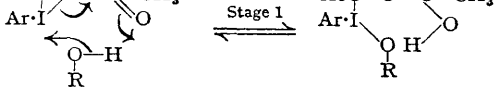
The results obtained with different phenyl iodosoacetates and *iso*hydrobenzoin in acetic acid are summarised below :

Substituent	*T*	$k \times 10^3$	$10^{-13}A$	*E* (kcal.)	Substituent	*T*	$k \times 10^3$	$10^{-13}A$	*E* (kcal.)
p-Me	34·7°	1·57, 1·61	36·3	21·6	*p*-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		
m-Me	34·7	1·77, 1·86	26·3	21·3	*m*-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	*m*-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 iodosoacetate. By analogy with the oxidation of glycols this reaction may proceed as follows :

$$\begin{tikzcd}
\mathrm{2PhI(OAc)_2 + 2Ar{\cdot}NH_2} \arrow[r, shift left] & \mathrm{2PhI(OAc)(NHAr) + 2AcOH} \arrow[l, shift left] \arrow[d, shift left] \\
\mathrm{2PhI(OAc)\,* + Ar{\cdot}NH{\cdot}NH{\cdot}Ar} \arrow[d] & \mathrm{2Ar{\cdot}NH\,* + 2PhI(OAc)\,*} \arrow[l] \arrow[u, shift left] \\
\mathrm{2PhI + 2AcOH + Ar{\cdot}N{:}N{\cdot}Ar} &
\end{tikzcd}$$

A preliminary investigation of the reaction of phenyl iodosoacetate with phenols in benzene solution has also yielded interesting results. At room temperature, *m*- and *p*-nitrophenol were rapidly oxidised, whereas *o*-nitrophenol remained unchanged. This further demonstrates the importance of hydrogen-bonding on the rate of reaction which has been discussed in the previous paper in relation to the relative rates of reaction of *cis*- and *trans*-glycols. The argument is more valid in the present instance as the reaction has been performed in benzene—a non-polar solvent. Thus the phenolic group in *o*-nitrophenol would be mainly hydrogen-bonded, whereas in the *m*- and *p*-compounds it would exist, at least partly, in the free state.

It was also found that phenyl iodosoacetate readily reacts with *iso*propyl alcohol, ethyl alcohol, and methyl alcohol in order of decreasing reactivity but is quite stable in *tert.*-butyl-alcoholic solution. This is in accord with the results obtained with the action of lead tetra-acetate on these compounds (see preceding paper).

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[*Received, May 13th,* 1952.]