[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. VIII. Decomposition of Substituted Diphenyliodonium Halides in Inert Solvents[1,2]

BY F. MARSHALL BERINGER AND MARVIN MAUSNER

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The effects of substituents on the first-order decomposition of diphenyliodonium halides in dimethylformamide are in accord with the picture of ion pairs decomposing by nucleophilic attack of the halide ion on the 1-carbon of the cation. The first-order rate constants in several solvents increased in the following order: diethylene glycol, dimethylformamide, nitrobenzene, benzene (fastest).

Several years ago the first-order decompositions of diphenyliodonium chloride, bromide and iodide in dimethylformamide were reported and compared with reactions in water, dioxane–water and diethylene glycol.[2,3] The present work is largely concerned with the effect of substituents[4] on the first-order rate constants and activation parameters for the decomposition of diphenyliodonium halides in dimethylformamide.[5] A brief comparison is also made of rates of decomposition in 2:3 dioxane–water, diethylene glycol, dimethylformamide, nitrobenzene and benzene.

Rate Constants in Dimethylformamide.[5]—First-order plots (log concentration of halide ion *versus* time) were usually linear to 90% reaction. The rate constants reported here were determined from essentially linear plots of runs completed 50% or more. The first-order rate constant for diphenyliodonium chloride at 60° was shown to be independent of initial concentration over the range 40–200 mmoles/kg.

Rate constants for symmetrically substituted diphenyliodonium halides are given in Table I and those for unsymmetrically substituted salts in Table II.

The data first show that in all cases studied the chlorides are least reactive, the bromides intermediate and the iodides most reactive, the order being that of increasing nucleophilicities of the halide ions.[3] Next, the data show that substituents have a large effect on the rates. Thus, relative rates for the decomposition of the bromides at 60° are, to take the extremes: 2-NO_2, 64; H, 1; 4,4′-$(CH_3O)_2$, 0.03. Indeed, throughout the series rates are increased by electron-attracting groups and decreased by electron-releasing groups. These groups may be arranged in order: (fastest) 2-NO_2 > 4-NO_2 > 3-NO_2 > HCl > *t*-butyl > cyclohexyl > CH_3 > F > CH_3O (slowest). Over-all this is the order to be expected for a reaction in which the halide ion makes a nucleophilic attack on the 1-carbon of the diphenyl-

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF SYMMETRICALLY SUBSTITUTED DIPHENYLIODONIUM HALIDES IN DIMETHYLFORMAMIDE

Substituents	X	100 k, hours^{-1} 60°	80°	100°	k/k_0,[a] 80°
3,3′-$(NO_2)_2$	Cl		18.7	184	2.5
	Br	1.22	19.6	211	2.0
	I		39		1.7
None[b]	Cl	0.47	7.6	91	1
	Br	0.54	10.0	104	1
	I	1.79	23.3	212	1
4,4′-Cl_2	Cl	0.294	5.46	67.5	0.72
	Br	0.471	7.7	80	.77
	I	1.38	20	218	.86
4,4′-(*t*-butyl)$_2$	Cl	0.187	3.12	34.1	0.41
	Br	.268	4.23	50.5	.42
	I	.697	10.3	126	.44
4,4′-$(C_6H_{11})_2$[c]	I	.45			
4,4′-$(CH_3)_2$	Cl		2.74	37.8	0.36
	Br	0.24	3.82	47.3	.38
	I	.31	6.9[d]		.30[d]
4,4′-F_2	Br	.105	17.3		.17
4,4′-$(CH_3O)_2$	Br	.0166	0.38	6.4	.038

[a] The ratio of rate constants of the substituted and unsubstituted salts having the same halide ion at 80°. [b] Figures from ref. 2. [c] C_6H_{11} is the cyclohexyl group. [d] Value is probably somewhat low.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF UNSYMMETRICALLY SUBSTITUTED DIPHENYLIODONIUM HALIDES IN DIMETHYLFORMAMIDE

Substituents	X	T, °C.	Hours^{-1} 100 k	k/k_0[a]
2-NO_2	Br	30.6	0.83	
		45	5.5	
		60	34.8	64
	I	60	134	75
3-NO_2	Br	80	18.9	1.9
4-NO_2	I	60	56.3	32
4-CH_3O	Br	80	5.1	0.51
	I	80	11.2	0.48

[a] The ratio of rate constants of the substituted and unsubstituted salts at the same temperature and having the same halide ion.

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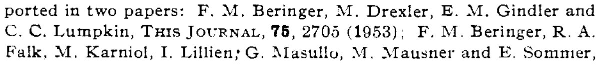
[1] This paper is taken from the dissertation of Marvin Mausner, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in 1956. The work has been reported in part at a Meeting of the American Chemical Society in Atlantic City in September, 1956 (Abstracts of Papers, p. 71-O).

[2] A continuation of the fourth paper in this series: F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

[3] Reference 2 presented a mechanism for the decomposition in dimethylformamide: . . . "the first-order kinetics obtained here suggest that in this solvent diphenyliodonium chloride existed largely as ion pairs. The rates at which these ion pairs decomposed to give products increased with the nucleophilicity of the halide ions, showing that the anions participated in the rate-determining step." This mechanism is used in the interpretation of the data of the present work.



[4] The synthesis of the substituted diphenyliodonium salts is reported in two papers: F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953); F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, *ibid.*, submitted.

[5] Kinetic runs, analyses and calculations were performed as in ref. 1.

iodonium cation, as here electron-withdrawing groups would stabilize the transition state more than the ground state while electron-releasing groups would stabilize the ground state more than the transition state.[3]

The data are not adequate for a full comparison of the effects of groups in one or both rings. The 3-nitro and 3,3′-dinitro salts seem to have about the same reactivity. That the deactivating effect of a 4-methoxyl group in one ring does not extend to the other ring is shown by the fact that the monosubstituted salts are about one-half as reactive as the parent unsubstituted salts.

Activation Parameters.[5]—Activation parameters for the decompositions of substituted diphenyliodonium halides are presented in Table III. It is seen that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are decreased strongly by the electron-accepting 2-nitro group but are increased by electron-releasing groups, especially the 4-methoxyl group.[6] Because of the variation of $\Delta S^{\ddagger}$, Hammett's σ–ρ relationship would not be expected to hold. The plot of log (k/k_0) *versus* σ was not linear and showed only the known rough correlation of rates with the tendencies of the groups to accept or release electrons.

Table III

Activation Parameters for the Decomposition of Substituted Diphenyliodonium Halides in Dimethylformamide

Substituents	X	Sec.$^{-1,a}$ log PZ	kcal.-mole$^{-1,b}$ E_a	ΔH^*	E.u.,^{c} ΔS^*
2-NO_2	Br	13.7	25.5	24.7	−3
3,3′-$(NO_2)_2$	Br	15.4	31.7	31.1	10
None	Cl	15.4	32.4	31.7	9
	Br	15.4	32.3	31.6	10
	I	13.9	29.3	28.6	3
4,4′-Cl_2	Cl	16.1	33.6	32.8	12
	Br	14.9	31.6^d	30.9^d	7
	I	15.1	31.2	30.5	8
4,4′-(*t*-butyl)$_2$	Cl	14.9	32.1	31.4	7
	Br	15.1	32.2	31.6	8
	I	15.4	32.0	31.3	9
4,4′-$(CH_3)_2$	Br	15.2	32.5	31.8	9
4,4′-$(CH_3O)_2$	Br	16.8	36.7	36.9	16
	I	16.9	36.1	35.4	16

[a] Units are for PZ, which was calculated for 80° (except 2-NO_2, 60°); estimated average error, ±0.3. [b] Estimated average error, ±0.5. [c] Estimated average error, ±2. [d] Estimated error, ±1.

Variation of Solvent.—The decomposition of diphenyliodonium halides in various non-aqueous or partially aqueous solvents occurred with first-order kinetics but at different rates; see Table IV.

Table IV

First-order Rate Constants for the Decomposition of Symmetrically Substituted Diphenyliodonium Halides in Various Solvents

Substituents	X	T, °C.	Solvent	100 k^b
None	Cl	98.3	2:3 Dioxane–water	0.6
			Diethylene glycol	2.0
			Dimethylformamide	80
4,4′-$(C_6H_{11})_2$^{a}	I	80	Dimethylformamide	0.45
			Nitrobenzene	5.3
			Benzene	8.7

[a] C_6H_{11} is cyclohexyl. [b] k in hours^{-1}.

There may be two factors operative in the observed decrease in the rate with increasing polarity of solvent. The first, and smaller, factor is that a significant part of the diphenyliodonium salt may in relatively polar media be present as unreactive free ions rather than as reactive ion pairs or quadrupoles.[2,7] This cannot be the major factor, however, as the kinetic order would tend to second if the salt were largely dissociated.[2,7]

The more important consideration, probably, is that each ion pair on reaction gives an activated complex which is less polar and thus less strongly solvated than the starting salt. Polar media, therefore, stabilize the starting material relative to the activated complex, increase the energy of activation and decrease the rate.

Cryoscopic Measurements.—Freezing point depression measurements for diphenyliodonium chloride in water (25–50 mmolar) gave a van't Hoff factor of 2.04 to be compared with one of 2.06 for sodium chloride in the same apparatus. Diphenyliodonium chloride is thus very largely dissociated in water.

More dilute solutions (15–25 mmolar) of 4,4′-dicyclohexyldiphenyliodonium iodide in benzene also were investigated. Here van't Hoff factors of about one-half were found (the average of four determinations was 0.515). Thus in this non-polar medium at about 5° the salt largely exists as quadrupoles. The large size of the cations may be a factor in repressing higher aggregates.

Since benzene at 80° has an even lower dielectric constant, it is probable that the decomposition of the 4,4′-dicyclohexyldiphenyliodonium iodide occurs by nucleophilic attack of iodide ion on a cation in a quadrupole of the salt.

Brooklyn 1, N. Y.

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(6) See J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(7) F. M. Beringer and E. M. Gindler, This Journal, **77**, 3200, 3203 (1955).