[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

The Thermal Decomposition of Benzoyl Peroxide

BY D. J. BROWN

In continuation of our studies[1] we investigated the effects of the temperature, of the solvent and of halide substitution on the benzene nucleus on the rate of decomposition of benzoyl peroxide.

The best procurable peroxides and solvents were further purified. *o*-Chlorobenzoyl peroxide alone was not obtained in the pure state; it appeared to contain some of the decomposition products. The purity of the peroxides was determined and the course of the decomposition was followed iodometrically.

In all cases, as previously observed[1], there was a preliminary period during which the rate of decomposition increased to a maximum. This was followed by two parallel reactions whose calculated order is n. The first order rate constant, k, as calculated from the observed molarity, $C - x$, the elapsed time and the initial observation, is included.

In Table I we have data representative of the results for the decomposition of benzene solutions of benzoyl peroxide in sealed bomb tubes at 90° ± 0.05.

TABLE I

DECOMPOSITION OF BENZOYL PEROXIDE IN BENZENE AT 90° ($n = 1.33$)

Time, min.	$(C - x)$ mole/l.	k min.$^{-1}$	$(C - x)$ mole/l.	k min.$^{-1}$
10	0.3260		0.1730	
20	.2902	0.0121	.1586	0.0087
30	.2624	.0111	.1479	.0078
40	.2307	.0107	.1302	.0094
60	.1935	.0105	.1107	.0089
80	.1563	.0106	.0921	.0090
120	.1070	.0102	.0670	.0085

When our values for the first order rate constants for tenth molar solutions in benzene at 80°, reported in the preceding paper,[1] and at 90° are included with those observed by Cohen[2] (starred in Table II), they extend his curve.

TABLE II

TEMPERATURE COEFFICIENT FOR THE DECOMPOSITION OF TENTH MOLAR BENZOYL PEROXIDE IN BENZENE

Temp., °C.	k, first order
*54°	1.83×10^{-6} sec.$^{-1}$
*64	5.84
*74	19.3
80	33.5
90	110

A number of series of observations were made for the thermal decomposition of benzoyl peroxide in nitrobenzene at 80 ± 0.05°. Representative data with the first order constants for two series are included in Table III.

TABLE III

DECOMPOSITION OF BENZOYL PEROXIDE IN NITROBENZENE AT 80°

Time, min.	$(C - x)$ mole/l.	k min.$^{-1}$	$(C - x)$ mole/l.	k min.$^{-1}$
30	0.1151		0.0358	
90	.0975	0.00277	.0311	0.00235
150	.0834	.00263	.0274	.00233
210	.0729	.00253	.0242	.00220
330	.0564	.00248	.0196	.00204

The calculated order of the reaction, n, for the range of concentrations in nitrobenzene which was studied, appear in Table IV. For each initial concentration of the series, $C - x_1$, the elapsed time for a third decomposition, Δt, is given.[1]

TABLE IV

ORDER OF REACTION OF THE DECOMPOSITION OF BENZOYL PEROXIDE IN NITROBENZENE AT 80°

$(C - x_1)$ mole/l.	Δt, min.	n
0.2835	120	
.1151	155	1.24
.0583	175	1.22
.0358	195	1.22
.0147	230	1.21

The first order rate constant for the decomposition of a tenth molar solution of benzoyl peroxide in the two solvents in relation to the dielectric constant, D, and the relative orders of reaction in these solvents are included in Table V.

TABLE V

RELATION OF RATE AND ORDER OF REACTION TO THE DIELECTRIC CONSTANT, 80°

Solvent	D	k min.$^{-1}$	n
Benzene	2.2	0.00201	1.29
Nitrobenzene	26.2	.00258	1.22

The rates of decomposition of several concentrations of three halogen substituted benzoyl peroxides in benzene as a solvent were observed at 80°. In Table VI we have included the ionization constant for each corresponding acid, K, the calculated rate constant for a tenth molar solution and the order of the reaction.

TABLE VI

DECOMPOSITION OF HALOBENZOYL PEROXIDES IN BENZENE, 80°

Solute, peroxide	K	k min.$^{-1}$	n
Benzoyl	6.6×10^{-5}	0.00201	1.29
p-Chloro	9.3	.00130	1.33
m-Bromo	13.7	.00156	1.18
o-Chloro	132	.0187	1.19

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(1) Brown, THIS JOURNAL, **62**, 2657 (1940).

(2) Cohen, *ibid.*, **67**, 17 (1945).

Discussion

The results presented in the preceding article[1] indicated that benzoyl peroxide in benzene, following a "preliminary period," decomposed as if two parallel reactions were occurring, a first order and a second order. This decomposition was interpreted as an initial dissociation of the peroxide followed by the further dissociation of the hemimer and the parallel reaction of the hemimer as an oxidizer. The final products of the reaction were determined by the reactions of the hemimer. The almost constant order of reaction with changing environment (Tables I, IV and V) and with halogen substitution on the benzene nucleus (Table VI) indicate a uniform mechanism of decomposition.

If the initial dissociation were ionic, $(RO)_2 = RO^+ + RO^-$, we would expect a large solvent effect on the rate of reaction in relation to the dielectric constant.[3] The increase in the rate of decomposition for a twelve-fold increase in the dielectric constant of the solvent is relatively small (Table V). The temperature coefficient for a reaction involving an ionized substance is usually relatively low.[3] The large variation of the rate constant with temperature and the comparative insensitivity to changes in dielectric constant may be further evidence that the decomposition proceeds via an uncharged radical mechanism, as was previously advanced[4,1] and is now accepted by many workers in the field.

The degree of the initial dissociation may be determined in part by the relative "negativity" of the radicals R and R′ of the peroxide R–O–O–R′ exactly as found by Gomberg[5] for the formation of trivalent carbon. The rate of reaction of the peroxide is determined by the degree of the dissociation which precedes and thus controls the subsequent rate determining reactions. Of those studied *o*-chlorbenzoyl peroxide decomposes the most rapidly. The rate constants for the *o*- and *p*-chlorobenzoyl peroxides have approximately the same ratio as the ionization constants of the two chlorobenzoic acids (Table VI), but no such simple relationship is found among the corresponding constants in the unsubstituted, *p*-chloro and *m*-bromo derivatives.

The data are correlated by the postulate that the initial reaction is a simple dissociation of the peroxide with the formation of radicals which contain monovalent oxygen as a constituent followed by two parallel reactions. The products of the decomposition are determined by these parallel reactions.

Summary

The rates of decomposition of benzoyl peroxide in benzene and the order of reaction at two temperatures are reported.

A study of the relation of the rate of reaction and order of reaction to the dielectric constant of the solvent was made.

The effect of substitution on the benzene nucleus of the benzoyl peroxide was studied.

(3) Walden, *Z. physik. Chem.*, **54**, 129 (1905), and later.

(4) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(5) Gomberg, *ibid.*, **1**, 91 (1924).

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[CONTRIBUTION FROM THE LABORATORY OF C. A. WAMSER]

Hydrolysis of Fluoboric Acid in Aqueous Solution

BY CHRISTIAN A. WAMSER

Aqueous fluoboric acid, which is now commercially available in the form of a 40% concentrate, is prepared[1] by treating aqueous hydrofluoric acid with the calculated amount of boric acid according to the equation

$$4HF + H_3BO_3 = HBF_4 + 3H_2O$$

It has been well known that aqueous solutions of fluoboric acid are more or less strongly hydrolyzed depending on the dilution, temperature and length of time they have been standing after preparation. Such solutions always contain more H ion than can be accounted for by the fluoboric acid they are calculated to contain.

Any successful explanation of the net changes occurring on hydrolysis must be capable of accounting for the following experimentally observable facts:

(1) When four moles of hydrofluoric acid and one mole of boric acid are mixed in aqueous medium, an immediate sharp increase in conductance occurs and heat is evolved, yet the solution contains no fluoboric acid immediately after the preparation (no precipitate with nitron). The total titratable acidity (as measured by the volume of standard alkali consumed to the phenolphthalein end-point in the presence of mannitol) of such a mixture immediately after preparation corresponds to five equivalents of acid, the solution at the end-point containing only F^- and BO_2^- anions.

(2) After preparation, the fluoboric acid content gradually increases to a final (equilibrium) value, while the total acidity decreases to a definite value. The only anions present at the titration end-point are BF_4^-, F^- and BO_2^-.

(3) When a fluoboric acid concentrate (which is itself appreciably hydrolyzed) is diluted with water, the total acidity gradually increases to a final (equilibrium) value.

(1) F. Fischer and K. Thiele, *Z. anorg. Chem.*, **67**, 304 (1910).