THE KINETICS OF THE REACTIONS OF ACYL PEROXIDES WITH ALKALI IODIDES—I

THE REACTIONS OF AROYL PEROXIDES WITH POTASSIUM IODIDE

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Abstract—The kinetics of the reaction of benzoyl peroxide with potassium iodide in 95·1% and absolute ethanol at 11°, 20° and 30° has been studied. The reaction is of the first order with respect to the concentration of each reactant. Rates of sixteen substituted benzoyl peroxides conform to Hammett's law with negative ρ values. The mechanism of the reaction is discussed.

THE reduction of benzoyl peroxide with the iodide anion is commonly used for the determination of this peroxide, the stoichiometry being:[1]

$$(PhCO)_2O_2 + 2I^- \rightarrow 2PhCO_2^- + I_2$$
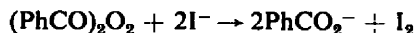
Although the application of this method to bis-(p-nitrobenzoyl) peroxide gives the correct result, in a similar determination of bis-(p-methoxybenzoyl) peroxide a satisfactory analysis was not obtained unless the reaction time was prolonged. This observation prompted an investigation into the kinetics of the mechanism of this reaction and the effect of the substituents on the reaction rate. The following report outlines the results obtained.

EXPERIMENTAL

Reagents. KI was recrystallized 3 times from aqueous EtOH (Found: I, 76·30. Calc. for KI: 76·45%.) Benzoyl peroxide was purified by dissolving in CHCl₃ kept at 40°, filtering the solution through a hot-water funnel into cold MeOH, collecting the precipitates after being cooled overnight, and drying in a vacuum desiccator, m.p. 106°. The purity was determined to be 99·96% by Bartlett's method.[2]

Fifteen symmetrically substituted benzoyl peroxides were synthesized from the corresponding substituted benzoyl chlorides according to the directions by Price and Krebs for bis-(p-nitrobenzoyl) peroxide.[3] The acid chlorides were prepared by heating under reflux the corresponding acids with thionyl chloride for 2 to 5 hr and fractional distillation of the product. p-Nitro- and p-bromobenzoyl chlorides were obtained by reaction with PCl₅ according to Adams and Jenkins' method.[4] Each peroxide was purified and assayed by the methods used for non-substituted benzoyl peroxide. Table 1 shows the decomposition points of the substituted benzoyl peroxides. An asymmetrically substituted peroxide, p-methoxy-p'-nitrodibenzoyl peroxide, was obtained by Leffler's method.[5]

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[1] a V. R. Kokatnur and M. Jelling, *J. Amer. Chem. Soc.* **63**, 1432 (1941); b K. Nozaki, *Analyt. Chem.* **18**, 583 (1946).
[2] P. D. Bartlett and R. Altschul, *J. Amer. Chem. Soc.* **67**, 817 (1945).
[3] C. C. Price and E. Krebs, *Organic Syntheses* Coll. Vol. III; p. 649. J. Wiley, New York (1955).
[4] R. Adams and R. L. Jenkins, *Organic Syntheses* Coll. Vol. I; p. 394. J. Wiley, New York (1956).
[5] J. E. Leffler, *J. Amer. Chem. Soc.* **72**, 67 (1950).

EtOH was chosen as a suitable solvent, since it does not react with I_2 at room temp and air has no effect on the reaction in this solvent.[1a]

A preliminary test showed that a trace of water in the solvent had a marked retarding effect on the rate of reaction. In order to obtain reproducible results, 95·1% EtOH or absolute ethanol was used. This was prepared by dehydrating commercial 99% EtOH with $(EtO)_2Mg$ and fractional distillation through a Vigreux column 60 cm in ht.

Kinetic measurements. The reaction was carried out in a colorimeter thermostatically controlled at a specified temp and the liberated I_2 was determined photometrically. Under these experimental conditions almost all the I_2 exists as the I_3^- ion, the equilibrium constant of the reaction $I_2 + I^- \rightleftharpoons I_3^-$ being about $2·7 \times 10^2$ at $29·5°$.
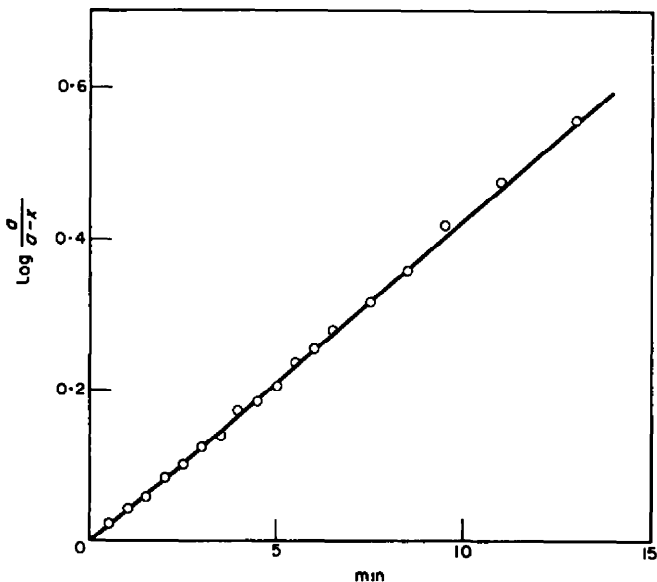

FIG. 1. A kinetic run of the reaction of benzoyl peroxide with potassium iodide in ethanol at $29·5°$

a and $a - x$: concentrations of benzoyl peroxide at time zero and t, respectively.

The spectrum of the I_3^- ion in EtOH, measured by a Beckman Model DU spectrophotometer, has a maximum absorption at wave length of 360 mμ; therefore, the light filtered through a Mazuda UV-D2 filter, which has a characteristic transmission ranging from 320 to 400 mμ, was used for measurements.

In EtOH, Lambert-Beer's law was obeyed between the I_3^- ion concentration up to $1·5 \times 10^{-5}$ g ion/l. and its optical density measured by the colorimeter in the presence of KI in the concentration of $5·0 \times 10^{-2}$ mol/l. I_2 concentration at time t, X_t, therefore, is given by the following equation:

$$X_t = -1/\varepsilon \log (I_t/I_o)$$

where I_o and I_t are the readings of the colorimeter at time zero and t, respectively, and ε is an apparent molecular extinction coefficient.

A solution (2 ml) of benzoyl peroxide in EtOH was added, by means of a pipette, to a solution (23 ml) of KI in EtOH placed in a cuvette in the thermostated colorimetric apparatus, both solutions being of known concentrations and previously heated to the same temp as the thermostat. The time at which half of the benzoyl peroxide solution had been discharged from the pipette was taken as the zero time of the reaction.

Fig. 1 illustrates a typical run at $29·5°$, indicating the first order kinetics of the reaction with respect to the concentration of benzoyl peroxide when KI is in large excess over benzoyl peroxide.

The rate law of a pseudo-first order having been thus established, all measurements thereafter

were made according to Guggenheim's method.[6,7] X_t and $X_{t+\tau}$, the concentrations of I_2 at time t and $t + \tau$, respectively, are related by the equation:

$$X_{t+\tau} - X_t = Ae^{-kt}$$

where k is apparent first order rate constant and A, a constant depending on the initial concentration and $k\tau$. Using I_t and $I_{t+\tau}$, the readings of the colorimeter at time t and $t + \tau$, this equation is re-written as:

$$\log (\log I_t - \log I_{t+\tau}) = A' - 0.4343kt$$

Usually two or three times the half-life of the reaction was taken as τ. Figure 2 shows a plot of the data obtained in absolute EtOH at 29.5° according to the above equation.
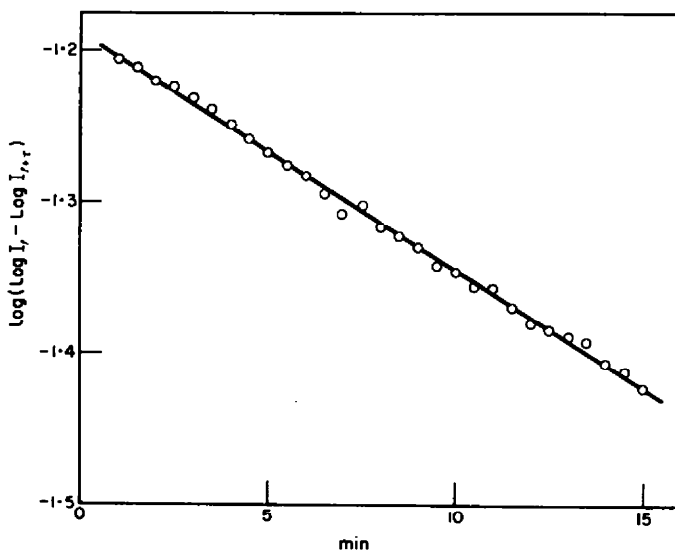

FIG. 2. The Guggenheim plot of a reaction of benzoyl peroxide with potassium iodide in ethanol at 29.5°

RESULTS AND DISCUSSION

Evidence for the absence of a photochemical reaction. Experiments, the results of which are shown in Table 2, demonstrate that the reaction is neither accelerated nor retarded by the light used for colorimetry.

Rate law and mechanism of the reaction. Figure 3 shows the relation between k obtained from the plot as explained above, an apparent first order rate constant when the iodide was in excess, and the initial concentration of the peroxide. The constancy of k shown here is an indication that no induced decomposition of benzoyl peroxide is involved.

A linear relation between k and the initial concentration of potassium iodide, as shown in Fig. 4, indicates that the rate of the reaction is of the first order in the concentration of potassium iodide. The kinetic measurements thus show that the rates of the reactions in both absolute and 95.1 % ethanol are represented by:

$$\text{Rate} = k_2[\text{Bz}_2\text{O}_2][\text{KI}]$$

[6] E. A. Guggenheim, *Phil. Mag.* **2**, 583 (1926).
[7] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* p. 49. J. Wiley, New York (1961).

TABLE 1. SUBSTITUTED BENZOYL PEROXIDES USED

Substituent	B.p. of acid chloride, °C	Decomposition point of peroxide, °C
Bis-(p-methoxy)	150–2/18 mm	127·5
Bis-(p-methyl)	100–2/15 mm	140·0
Bis-(p-t-butyl)	98–100/18 mm	142·5
Bis-(p-fluoro)	93–5/18 mm	98·5
Bis-(p-chloro)	109–112/18 mm	142·5
Bis-(p-bromo)	132–5/17 mm	149·5
Bis-(p-iodo)	155–7/26 mm	159·5
Bis-(p-nitro)	152–4/20 mm	158·0
Bis-(m-nitro)	153–5/18 mm	138·0
Bis-(m-methoxy)	130–2/30 mm	85·0
Bis-(m-methyl)	120–1/20 mm	54·0
Bis-(m-fluoro)	94–6/20 mm	88·0
Bis-(m-chloro)	125–7/40 mm	125·0
Bis-(m-bromo)	138–140/30 mm	131·0
Bis-(m-iodo)	143–5/20 mm	125·0
Bis-(m-cyano)	150–2/18 mm	153·0
p-Methoxy-p'-nitro		108·0

TABLE 2. EVIDENCE FOR ABSENCE OF A
PHOTOCHEMICAL REACTION

The reaction was carried out in ethanol at 29·5°
The initial concentrations

$[KI] = 4·999 \times 10^{-3}$ mol/l.
$[Bz_2O_2] = 1·587 \times 10^{-5}$ mol/l.

Under ordinary conditions		The photometer light source was off during the initial 10 min	
t(min)	I_t	t(min)	I_t
0	80·7	0	80·4
10·0	68·9	10·0	
15·0	66·8	15·0	66·0
20·5	65·3	20·5	64·8
21·0	65·2	21·0	64·6
22·0	65·1	22·0	64·5
23·0	65·0	23·0	64·4
24·0	64·9	24·0	64·2
25·0	64·8	25·0	64·1
26·0	64·7	26·0	64·0
27·0	64·5	27·0	64·0
28·0	64·5	28·0	63·9
29·0	64·4	29·0	63·8
30·0	64·3	30·0	63·7

TABLE 3. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION
BETWEEN BENZOYL PEROXIDE AND POTASSIUM IODIDE

Solvent	Temp. °C	k_2 (1 mol^{-1} sec^{-1})	A (1 mol^{-1} sec^{-1})	E_a (kcal/mol)	$\Delta H\ddagger$ (kcal/mol)	$\Delta S\ddagger$ (E.U.)
Absolute ethanol	29·5	0·444 ± 0·004	$(6·2 \pm 1·9) \times 10^6$	12·6 ± 0·4	12·0 ± 0·4	−20·4 ± 1·4
	20·5	0·248 ± 0·004				
	11·0	0·112 ± 0·006				
95·1% ethanol	29·5	0·213 ± 0·002	$(1·0 \pm 0·6) \times 10^7$	10·7 ± 0·7	10·1 ± 0·7	−28·4 ± 2·6
	20·5	0·128 ± 0·004				
	11·0	0·0659 ± 0·0013				

This rate law is readily derived by assuming the following reaction sequence:

$$C_6H_5COOOCOC_6H_5 + K^+I^- \xrightarrow{k_2} C_6H_5COOK + C_6H_5COO\cdot + I\cdot \qquad (1)$$

$$C_6H_5COO\cdot + K^+I^- \longrightarrow C_6H_5COOK + I\cdot \qquad (2)$$

$$2I\cdot \longrightarrow I_2 \qquad (3)$$

Reaction (1) being regarded as the rate determining process and reactions (2) and (3) as fast reactions, the usual stationary state method gives:

$$-d[Bz_2O_2]/dt = d[I_2]/dt = k_2[Bz_2O_2][KI]$$

k_2 is the rate constant for reaction (1), which is considered to be a reductive cleavage reaction involving an electron transfer from an iodide ion to the O–O linkage of benzoyl peroxide.

An obvious alternative mechanism cannot be excluded, in which benzoyl peroxide and the iodide ion give hypothetical benzoyl hypoiodite[8] and a benzoate ion in an initial rate determining step with a subsequent rapid collapse of the hypoiodite either with the iodide ion to yield a molecule of iodine and a benzoate anion or by itself to give a benzoxy radical and an iodine atom.

Activation parameters. The energy of activation E_a and the frequency factor A were calculated by using the Arrhenius equation by the method of least squares. The enthalpy of activation $\Delta H\ddagger$, and the entropy of activation $\Delta S\ddagger$, were calculated from the above activation energy by the usual method.[9] The results are summarized in Table 3.

The rate of the reaction in absolute ethanol is twice as fast as in 95·1% ethanol as shown in Table 3. On the other hand, the enthalpy of activation is higher in absolute ethanol than in 95·1% ethanol. It is interesting to note that the decrease in rate in 95·1% ethanol is mainly caused by decrease in the entropy of activation.

[8] R. G. Johnson and R. K. Ingham, *Chem. Revs.* **56**, 219 (1956); M. Anbar and D. Ginsburg, *Ibid.* **54**, 925 (1954).

[9] Ref. 7, p. 99.

TABLE 4. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTIONS BETWEEN DISUBSTITUTED BENZOYL PEROXIDES AND POTASSIUM IODIDE IN ABSOLUTE ETHANOL

Substituents	Temp. °C	k_2 (1 mol^{-1} sec^{-1})	$\Delta H\ddagger$ (kcal/mol)	$\Delta S\ddagger$ (E.U.)
Bis(p-methoxy)	11·0	0·0639 ± 0·0022	14·9 ± 0·7	−11·4 ± 2·5
	20·5	0·152 ± 0·009		
	29·5	0·345 ± 0·024		
Bis(p-nitro)	20·5	3·93 ± 0·15	14·5 ± 0·4	−6·6 ± 1·5
	29·5	8·44 ± 0·05		
Bis(p-fluoro)	11·0	0·161 ± 0·005	16·4 ± 0·2	−4·3 ± 0·8
	20·5	0·435 ± 0·004		
	29·5	1·023 ± 0·012		
Bis(p-chloro)	11·0	0·289 ± 0·007	13·6 ± 0·3	−13·1 ± 1·2
	20·5	0·675 ± 0·017		
	29·5	1·35 ± 0·04		
Bis(p-bromo)	11·0	0·352 ± 0·004	12·9 ± 0·5	−15·2 ± 1·9
	20·5	0·773 ± 0·035		
	29·5	1·53 ± 0·06		
Bis(p-iodo)	11·0	0·337 ± 0·000	14·8 ± 0·6	−8·6 ± 1·9
	20·5	0·723 ± 0·026		
	29·5	1·69 ± 0·01		
Bis(p-methyl)	11·0	0·0595 ± 0·0005	16·8 ± 0·5	−5·0 ± 1·8
	20·5	0·180 ± 0·000		
	29·5	0·393 ± 0·005		
Bis(p-t-butyl)	11·0	0·0622 ± 0·0004	16·2 ± 0·3	−7·6 ± 1·1
	20·5	0·175 ± 0·002		
	29·5	0·385 ± 0·002		
p-Methoxy, p′-nitro	11·0	0·308 ± 0·002	16·0 ± 0·7	−4·5 ± 2·2
	20·5	0·663 ± 0·007		
	29·5	1·80 ± 0·02		
Bis(m-methoxy)	20·5	0·211 ± 0·003	14·8 ± 0·4	−11·1 ± 1·5
	29·5	0·462 ± 0·009		
Bis(m-methyl)	20·5	0·157 ± 0·006	14·7 ± 0·6	−12·1 ± 2·1
	29·5	0·342 ± 0·006		
Bis(m-fluoro)	20·5	0·912 ± 0·001	13·0 ± 0·4	−14·4 ± 1·3
	29·5	1·813 ± 0·031		
Bis(m-chloro)	20·5	1·186 ± 0·026	13·9 ± 0·5	−10·8 ± 1·8
	29·5	2·477 ± 0·038		
Bis(m-bromo)	20·5	1·207 ± 0·029	14·1 ± 0·5	−10·0 ± 1·7
	29·5	2·553 ± 0·033		
Bis(m-iodo)	20·5	1·143 ± 0·014	13·1 ± 0·3	−13·6 ± 0·9
	29·5	2·292 ± 0·012		
Bis(m-nitro)	20·5	4·57 ± 0·23	13·9 ± 0·8	−8·3 ± 2·6
	29·5	9·489 ± 0·032		

The effect of substituents. The results of kinetic measurements with p- and m-substituted benzoyl peroxides are summarized in Tables 4 and 5. Figures 5 and 6 show plots of log k_2 versus $\Sigma\sigma$, where k_2 is the second order rate constant of the reaction at 20·5° and $\Sigma\sigma$ is the sum of Hammett's constants[10] for the substituents involved.

[10] H. H. Jaffé, *Chem. Revs.* **53**, 191 (1953).

TABLE 5. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTIONS
BETWEEN DISUBSTITUTED BENZOYL PEROXIDES AND POTASSIUM IODIDE
IN 95% ETHANOL

Substituents	Temp. °C	k_2 (1 mol^{-1} sec^{-1})	$\Delta H\ddagger$ (kcal/mol)	$\Delta S\ddagger$ (E.U.)
Bis(p-methoxy)	11·0	0·0394 ± 0·0005	12·6 ± 0·4	−20·5 ± 1·4
	20·5	0·0791 ± 0·0003		
	29·5	0·163 ± 0·004		
Bis(p-nitro)	11·0	1·59 ± 0·02	14·0 ± 0·7	−8·3 ± 2·2
	20·5	3·19 ± 0·17		
	29·5	7·63 ± 0·00		
Bis(p-fluoro)	11·0	0·106 ± 0·002	14·0 ± 0·5	−13·6 ± 1·7
	20·5	0·265 ± 0·004		
	29·5	0·523 ± 0·018		
Bis(p-chloro)	20·5	0·422 ± 0·013	15·9 ± 0·7	−5·6 ± 2·3
	29·5	0·977 ± 0·014		
Bis (p-bromo)	20·5	0·501 ± 0·001	14·2 ± 0·1	−11·5 ± 0·3
	29·5	1·060 ± 0·004		
Bis(p-iodo)	20·5	0·492 ± 0·003	9·3 ± 0·4	−28·2 ± 1·4
	29·5	0·812 ± 0·012		
Bis(p-methyl)	20·5	0·0984 ± 0·0005	14·3 ± 0·5	−14·6 ± 1·5
	29·5	0·191 ± 0·001		
	40·0	0·475 ± 0·009		
Bis(p-t-butyl)	20·5	0·0914 ± 0·0024	14·0 ± 0·3	−15·3 ± 1·2
	29·5	0·209 ± 0·005		
	40·0	0·439 ± 0·005		
p-Methoxy, p′-nitro	11·0	0·181 ± 0·016	16·8 ± 1·0	−2·7 ± 3·5
	20·5	0·423 ± 0·003		
	29·5	1·22 ± 0·01		
Bis(m-methoxy)	20·5	0·135 ± 0·004	14·1 ± 0·6	−14·5 ± 2·2
	29·5	0·284 ± 0·004		
Bis(m-methyl)	20·5	0·096 ± 0·001	12·4 ± 0·3	−20·8 ± 1·2
	29·5	0·186 ± 0·002		
Bis(m-fluoro)	20·5	0·583 ± 0·012	14·1 ± 0·7	−12·4 ± 2·2
	29·5	1·241 ± 0·020		
Bis(m-chloro)	20·5	0·721 ± 0·048	13·4 ± 1·5	−13·5 ± 5·2
	29·5	1·458 ± 0·053		
Bis(m-bromo)	20·5	0·804 ± 0·018	13·4 ± 0·6	−13·4 ± 2·0
	29·5	1·635 ± 0·026		
Bis(m-iodo)	20·5	0·629 ± 0·020	15·5 ± 0·7	−6·7 ± 2·3
	29·5	1·422 ± 0·012		
Bis(m-nitro)	20·5	4·482 ± 0·084	13·0 ± 0·5	−11·6 ± 2·5
	29·5	8·21 ± 0·15		

The reaction constants in Hammett's equations were evaluated by the method of least squares to be:

$$\rho = 0.756 \pm 0.034 \text{ in absolute ethanol}$$

and

$$\rho = 0.867 \pm 0.051 \text{ in } 95.1\% \text{ ethanol;}$$

the errors attached are standard errors.

The correlation between $\Sigma\sigma$ and $\log k_2$ is good, the correlation coefficient[11] being 0·976 in absolute ethanol and 0·978 in 95·1% ethanol.

[11] P. G. Hoel, *Introduction to Mathemathical Statistics* p. 85. J. Wiley, New York (1949).
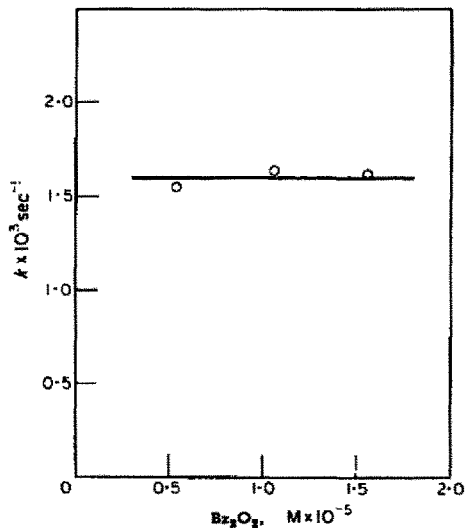
Fig. 3. Observed first-order rate constants at various initial concentrations of benzoyl peroxide at 29·5°
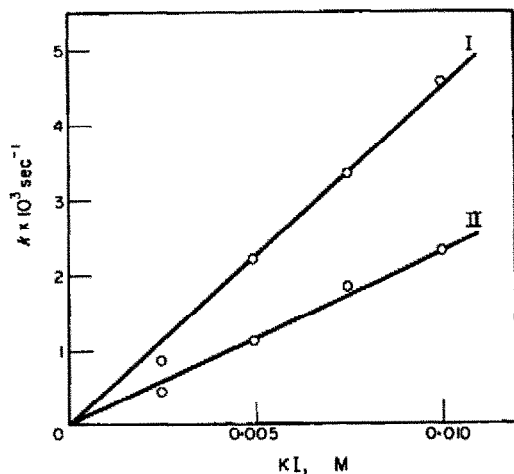

Fig. 4. Observed first-order rate constants at various concentrations of potassium iodide at 29·5°

I: in ethanol;   II: in 95% ethanol

The values of k_2 for p-methoxy-p'-nitrodibenzoyl peroxide are 0·663 in absolute ethanol, and 0·423 in 95·1% ethanol at 20·5°. Figures 5 and 6 show that these values fall on the Hammett plot when the sum of the substituent constants for the p-nitro and the p-methoxy group is used for $\Sigma\sigma$.

According to the mechanism set forth above, an electron-withdrawing substituent must increase the rate of the reaction, since this type of substituent should make it easier for an electron to be transferred from the iodide ion to the substituted benzoyl peroxide. The positive value for ρ obtained here is consistent with this mechanism.
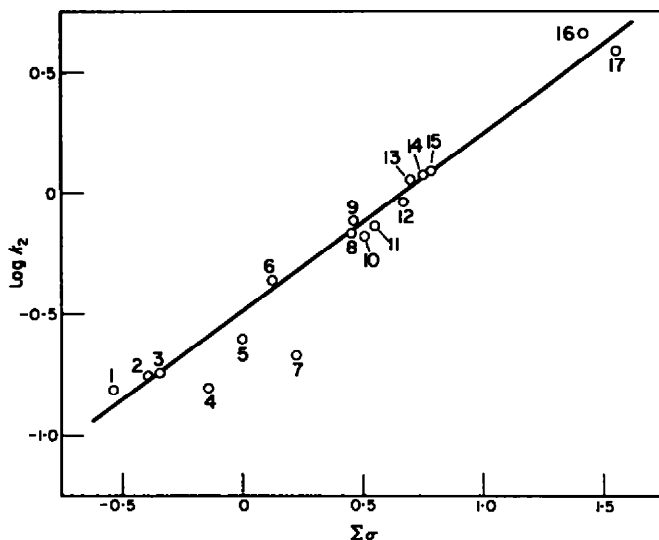
FIG. 5. The Hammett plot of the rate constants for substituted benzoyl peroxides in absolute ethanol at 20·5°

1: *p*-MeO, 2: *p*-t-Bu, 3: *p*-Me, 4: *m*-Me, 5: H, 6: *p*-F, 7: *m*-MeO, 8: *p*-Cl, 9: *p*-Br, 10: *p*-NO₂, *p'*-MeO, 11: *p*-I, 12: *m*-F, 13: *m*-I, 14: *m*-Cl, 15: *m*-Br, 16: *m*-NO₂, 17: *p*-NO₂
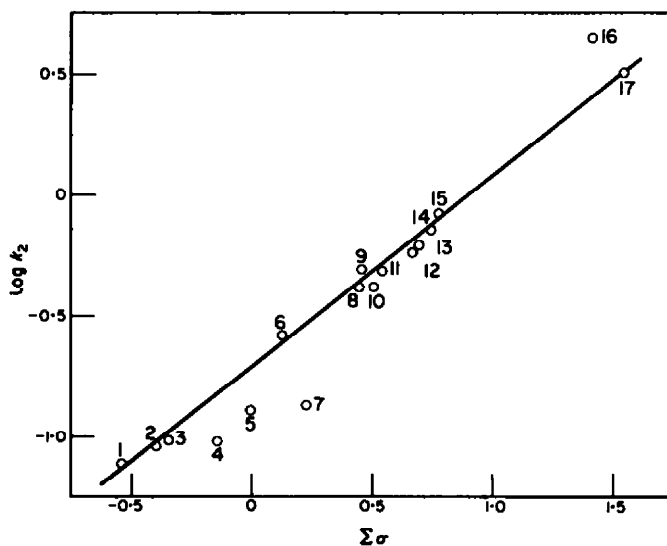

FIG. 6. The Hammett plot of the rate constants for substituted benzoyl peroxides in 95% ethanol at 20·5°

1: *p*-MeO, 2: *p*-t-Bu, 3: *p*-Me, 4: *m*-Me, 5: H, 6: *p*-F, 7: *m*-MeO, 8: *p*-Cl, 9: *p*-Br, 10: *p*-NO₂, *p'*-MeO, 11: *p*-I, 12: *m*-F, 13: *m*-I, 14: *m*-Cl, 15: *m*-Br, 16: *m*-NO₂, 17: *p*-NO₂

The fact that the Hammett relation holds with a compound with two different substituents, when the sum of the substituent constants are used, seems to suggest that an electron is transferred to the vacant anti-bonding orbital of the O–O bond, resulting in the transition state leading to the rupture of this bond.

Swain *et al.* reported $\rho = -0.38$ for the thermal decomposition at 80° of substituted benzoyl peroxides in dioxan which was 0·2 M in 3,4-dichlorostyrene.[12] On the other hand Imoto and Choe studied the reaction between substituted benzoyl peroxides and dimethylaniline and the reaction constant was found to be $+0.181$.[13] The reactions of the peroxides with dimethylaniline and with potassium iodide are considered to belong to the same category, that is, a reductive cleavage reaction of benzoyl peroxide, since they have ρ of the same sign.

A plot of the data for *meta* substituents alone gives better straight lines with

$$\rho = 0.972 \pm 0.081 \text{ in absolute ethanol (correlation coefficient, } 0.984)$$

and

$$\rho = 1.098 \pm 0.070 \text{ in } 95.1\% \text{ ethanol (correlation coefficient, } 0.992).$$

It is apparent on inspection of Figs. 5 and 6 that the points for *para* substituents deviate upwards from these *meta* lines, suggesting that more positive values should be used for constants for the *para* substituents, in order for a better fit to be obtained. The reason seems to be as follows: A mesomerically electron-releasing group, such as a methoxy group, at the *para* position in benzoic acid stabilizes the undissociated acid molecule by conjugation with the carbonyl group, whereas this effect is small, if at all, in the dissociated anion, thus tending to make the σ value more negative than if the electron-releasing effect were absent. In the transition state of the reaction under consideration, such a conjugative effect will still persist, since the negative charge is not yet developed on the oxygen atom to the same extent as in the carboxylate anion, the net result being that the polar effect by such a group should be more positive than the Hammett σ constant suggests.

[12] C. G. Swain, W. H. Stockmayer and J. T. Clark, *J. Amer. Chem. Soc.* **72**, 5426 (1950).
[13] M. Imoto and S. Choe, *J. Polymer Sci.* **15**, 485 (1955).