

**960. Oxidation of Organic Sulphides. Part X.\* Acid-catalysis in the Oxidation of Organic Sulphides by Peroxybenzoic Acid in Aprotic Non-basic Solvents.**

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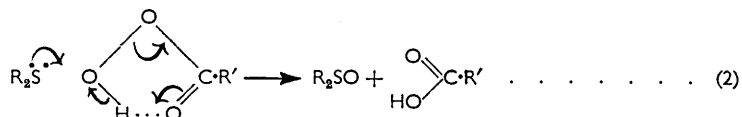
The oxidation of aryl sulphides by peroxybenzoic acid is catalyzed by trifluoroacetic acid in carbon tetrachloride and in benzene, but not in dioxan. Benzoic acid, which is formed during the reaction, strongly inhibits the catalytic effect; when the inhibition is allowed for, the kinetics of the catalyzed reaction are described by the equation

$$\text{Rate} = k[\text{R}_2\text{S}][\text{R}'\text{-CO}_3\text{H}] + k'[\text{R}_2\text{S}][\text{R}'\text{-CO}_3\text{H}][\text{CF}_3\text{-CO}_2\text{H}].$$

It is generally accepted<sup>1-3</sup> that organic sulphides are oxidized by hydrogen peroxide, alkyl hydroperoxides, and peracids in a heterolytic process involving nucleophilic attack of sulphur upon oxygen:



In the oxidation by peroxyacids the effect of solvents and of salts on the rate has been taken to imply the transference of the proton in a cyclic process involving intramolecularly hydrogen-bonded peracid:



As part of our studies of the oxidation of organic sulphides and sulphoxides<sup>3</sup> and of the more general work in this Department,<sup>4</sup> we now report an investigation of acid-catalysis in the oxidation of aryl sulphides to sulphoxides by peroxybenzoic acid. Little is known of this catalysis, except that weak acids are without effect,<sup>1-3,5</sup> while stronger acids appear to be catalysts, particularly in aprotic solvents.<sup>6,7</sup>

## RESULTS

The reaction between peroxybenzoic acid and *p*-nitrodiphenyl sulphide or *pp'*-dinitrodiphenyl sulphide in the presence of trifluoroacetic acid was followed kinetically. The nitro-groups reduce the nucleophilic power of the sulphides,<sup>3a</sup> and lead to a reaction rate that can be measured conveniently. Dioxan, benzene, and carbon tetrachloride were used as solvents.

The stoichiometry of the reaction has been investigated by other authors<sup>1</sup> and by us<sup>3</sup> for a variety of systems; the oxidation is a two-step reaction,  $\text{>S} \longrightarrow \text{>SO} \longrightarrow \text{>SO}_2$ , where the first stage is much faster than the second, so that the latter does not interfere with the kinetics of the former (except, in some cases, in the last part of the reaction). Nevertheless the products of the reaction in kinetic conditions have been isolated; at completion they were benzoic acid and sulphoxide, with ~8% of sulphide and sulphone.

*Reaction in Dioxan.*—The reaction between *p*-nitrodiphenyl sulphide ( $\sim 1.8 \times 10^{-2}\text{M}$ ) and

\* Part IX, *Ricerca sci.*, 1960, **30**, 1788.

<sup>1</sup> Barnard, Bateman, and Cummins, "Organic Sulphur Compounds," ed. Kharasch, Pergamon Press, London, 1961, p. 229.

<sup>2</sup> Overberger and Cummins, *J. Amer. Chem. Soc.*, 1953, **75**, 4250, 4783.

<sup>3</sup> Modena *et al.*, *Gazzetta*, (a) 1957, **87**, 1906; 1959, **89**, (b) 834, (c) 843; 1960, **80**, (d) 3, (e) 12, (f) 382, (g) 621, (h) 682; (i) *Ricerca sci.*, 1960, **30**, 128.

<sup>4</sup> Mangini, *J. Chim. phys.*, 1959, **240**; *Boll. Sci. Fac. Chim. ind. Bologna*, 1960, **28**, 191.

<sup>5</sup> Lynch and Pausaker, *J.*, 1955, 1525.

<sup>6</sup> Swern, "Organic Reactions," ed. Adams, Wiley and Sons, New York, 1953, Vol. VII, 378.

<sup>7</sup> Berti *et al.*, *Gazzetta*, 1959, **89**, 2380; 1960, **90**, 1763; *J. Org. Chem.*, 1960, **25**, 1286.

peroxybenzoic acid ( $\sim 1.4 \times 10^{-2}M$ ) in dioxan was clearly of the second order. No acid-catalysis was detected, even when the concentration of trifluoroacetic acid was as high as  $5 \times 10^{-1}M$  (see Table 1).

*Reaction in Carbon Tetrachloride.*—In this solvent, benzoic acid (up to  $10^{-1}M$ ) had no effect on the rate, but trifluoroacetic acid was catalytic even at  $0.6 \times 10^{-2}M$  (see Table 2). Initial

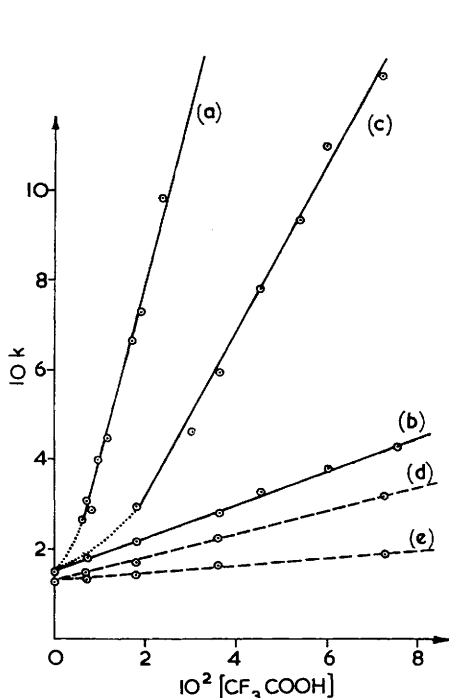


FIG. 1.

FIG. 1. Solvent: Carbon tetrachloride.\* (a) No benzoic acid added; (b) benzoic acid in large excess ( $14 \times 10^{-2}M$ ); (c) benzoic acid at intermediate concentration ( $3 \times 10^{-2}M$ ). Solvent: Benzene. (d) No benzoic acid added; (e) benzoic acid in large excess ( $14 \times 10^{-2}M$ ).

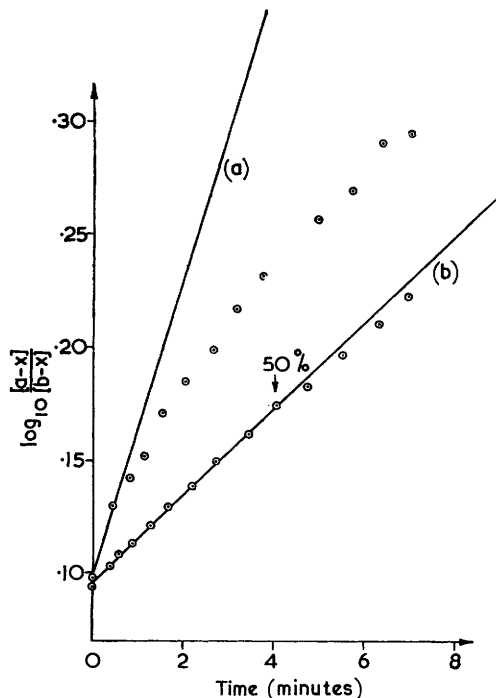


FIG. 2.

FIG. 2. Typical runs in carbon tetrachloride; (a) no benzoic acid added (*p*-nitrodiphenyl sulphide  $1.79 \times 10^{-2}M$ ; peroxybenzoic acid  $1.43 \times 10^{-2}M$ ; trifluoroacetic acid  $3.64 \times 10^{-2}M$ ); (b) benzoic acid in large excess (*p*-nitrodiphenyl sulphide  $1.79 \times 10^{-2}M$ ; peroxybenzoic acid  $1.44 \times 10^{-2}M$ ; trifluoroacetic acid  $1.82 \times 10^{-2}M$ ; benzoic acid  $14.0 \times 10^{-2}M$ ).

\* The initial point (uncatalyzed rate) is a little outside the line (a); it is probably due to the small quantity of benzoic acid always present with peroxybenzoic acid. The main consequence of this fact is that the points of (a) are a little displaced because the "effective" concentration of  $CF_3 \cdot CO_2H$  is smaller than stoichiometric.

rates were calculated because the rate coefficient decreases with time; this effect is discussed below. The rate of the reaction increases linearly with the concentration of trifluoroacetic acid (see Fig. 1).

TABLE I.  
Reaction in dioxan at  $13.0^\circ$ .

Run no. ....	1	2	3	4	5
$[CF_3 \cdot CO_2H]$ ( $10^{-2}M$ ) .....	—	—	37.5	53.2	53.2
$10^2 k$ ( $\text{mole}^{-1} \text{sec.}^{-1}$ ) .....	5.93	5.97	5.97	6.02	5.91

The effect of benzoic acid on the trifluoroacetic-catalyzed reaction was then studied in detail. If the concentration of trifluoroacetic acid was held constant, increasing amounts of benzoic acid decreased the initial rate, until, with a large excess of benzoic acid, a limiting rate was reached. The reaction then follows a second-order rate equation, the plot of  $\log(a-x)/(b-x)$  against time being linear to 60% reaction (see Fig. 2). The relevant data are collected in Table 3. If benzoic acid was present in large excess, the rate increased with the concentration of trifluoroacetic acid, but less steeply than in the absence of benzoic acid (see Table 4 and Fig. 1).

TABLE 2.

Catalysis in the reaction of *p*-nitrodiphenyl sulphide with perbenzoic acid in carbon tetrachloride at 0.0° by benzoic and trifluoroacetic acid.

Run no. ....	6	7	8	9	10	11	12
[PhS·C <sub>6</sub> H <sub>4</sub> ·NO <sub>2</sub> - <i>p</i> ] (10 <sup>-2</sup> M) .....	1.35	1.80	1.81	1.79	1.80	1.79	1.79
[Ph·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	1.60	1.60	1.37	1.25	1.45	1.45	1.41
(Ph·CO <sub>2</sub> H) (10 <sup>-2</sup> M) .....	—	—	—	2.02	5.02	10.0	—
CF <sub>3</sub> ·CO <sub>2</sub> H (10 <sup>-2</sup> M) .....	—	—	—	—	—	—	0.58
10 <i>k</i> (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	1.44	1.49	1.51	1.45	1.49	1.55	2.60
Run no. ....	13	14	15	16	17	18	19
[PhS·C <sub>6</sub> H <sub>4</sub> ·NO <sub>2</sub> - <i>p</i> ] (10 <sup>-2</sup> M) .....	1.79	1.79	1.79	1.79	1.79	1.79	1.79
[Ph·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	1.40	1.49	1.35	1.41	1.41	1.36	1.46
(Ph·CO <sub>2</sub> H) (10 <sup>-2</sup> M) .....	—	—	—	—	—	—	—
CF <sub>3</sub> ·CO <sub>2</sub> H (10 <sup>-2</sup> M) .....	0.71	0.81	0.97	1.17	1.75	1.94	2.44
10 <i>k</i> (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	3.05	2.85	3.98	4.47	6.62	7.26	9.80

TABLE 3.

Reaction in carbon tetrachloride at 0.0°: effect of benzoic acid.

PhS·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>-*p* ~1.80 × 10<sup>-2</sup>M; Ph·CO<sub>2</sub>H ~1.4 × 10<sup>-2</sup>M; CF<sub>3</sub>·CO<sub>2</sub>H 1.80 × 10<sup>-2</sup>M.

Run no. ....	*	20	21	22	23
[R·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	—	1.90	3.15	8.42	14.0
10 <i>k</i> (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	7.0	2.95	2.67	2.30	2.17

\* Evaluated from data in Table 2.

TABLE 4.

Reaction in carbon tetrachloride at 0.0°: effect of excess of benzoic acid.

PhS·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>-*p* ~1.8 × 10<sup>-2</sup>M; Ph·CO<sub>2</sub>H ~1.4 × 10<sup>-2</sup>M; Ph·CO<sub>2</sub>H 14.0 × 10<sup>-2</sup>M.

Run no. ....	*	24	25	26	27	28	29
[CF <sub>3</sub> ·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	—	0.73	1.82	3.64	4.54	6.05	7.56
10 <i>k</i> (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	1.50	1.80	2.15	2.81	3.29	3.77	4.25

\* Average value from the data in Table 2.

If benzoic acid was present in limited amount and the concentration of trifluoroacetic acid was progressively increased, the rate of the reaction increased slowly until [CF<sub>3</sub>·CO<sub>2</sub>H] ≥ [Ph·CO<sub>2</sub>H]; then the rate coefficient increased almost as fast as in the absence of benzoic acid (see Table 5 and Fig. 1).

TABLE 5.

Reaction in carbon tetrachloride at 0.0°: effect of trifluoroacetic acid concentration.

PhS·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>-*p* ~1.8 × 10<sup>-2</sup>M; Ph·CO<sub>2</sub>H ~1.4 × 10<sup>-2</sup>M; Ph·CO<sub>2</sub>H 3.0 × 10<sup>-2</sup>M.

Run no. ....	30	31	32	33	34	35	36
[CF <sub>3</sub> ·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	1.82	3.03	3.64	4.54	5.45	6.05	7.28
10 <i>k</i> (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	2.93	4.61	5.93	7.80	9.32	10.96	12.55

*Reaction in Benzene.*—The results for *pp'*-dinitrodiphenyl sulphide in benzene solutions were substantially the same in outcome as above, but the acid catalysis was much smaller (see Table 6 and Fig. 1).

*Acid Strength of Trifluoroacetic Acid and Benzoic Acid in Carbon Tetrachloride and in Benzene.*—An approximate value of the acid strength of trifluoroacetic acid in benzene and in carbon tetrachloride in the absence and presence of benzoic acid was obtained by measuring

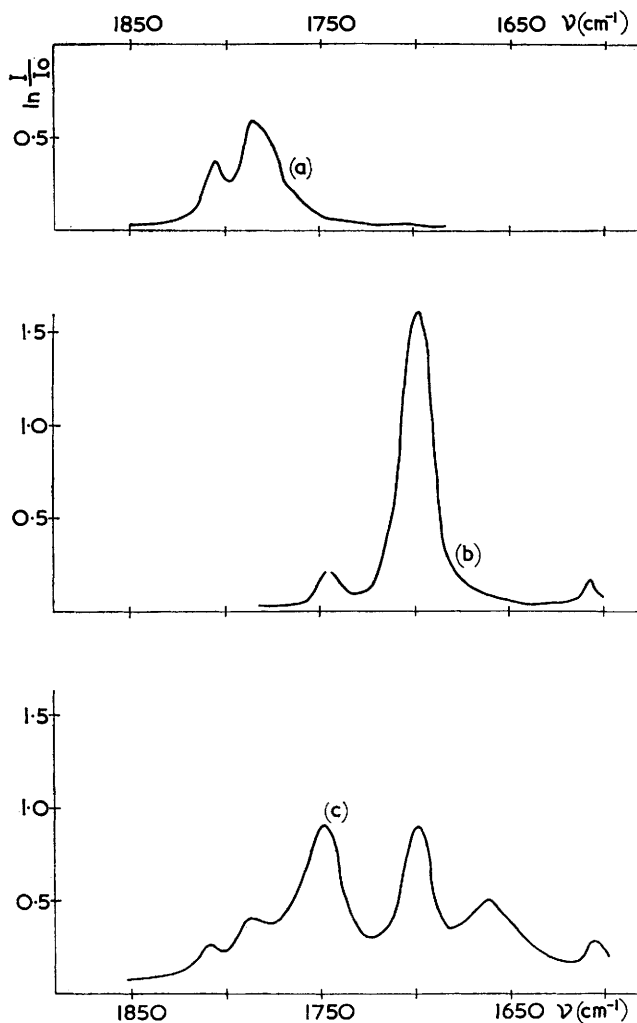


FIG. 3. Infrared spectra in carbon tetrachloride of: (a)  $\text{CF}_3\cdot\text{CO}_2\text{H}$  ( $9.5 \times 10^{-3}\text{M}$ ); (b)  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$  ( $9.5 \times 10^{-3}\text{M}$ ); (c)  $\text{CF}_3\cdot\text{CO}_2\text{H}$  ( $9.5 \times 10^{-3}\text{M}$ ) +  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$  ( $9.5 \times 10^{-3}\text{M}$ ).

TABLE 6.

Reaction in benzene at $13.0^\circ$ .										
$(p\text{-NO}_2\cdot\text{C}_6\text{H}_4)_2\text{S} \sim 1.8 \times 10^{-2}\text{M}$ ; $\text{Ph}\cdot\text{CO}_2\text{H} \sim 1.2 \times 10^{-2}\text{M}$ .										
Run no.....	37	38	39	40	41	42	43	44	45	46
$[\text{CF}_3\cdot\text{CO}_2\text{H}]$ ( $10^{-2}\text{M}$ )	—	0.72	1.81	3.63	7.26	—	0.73	1.81	3.63	7.30
$[\text{Ph}\cdot\text{CO}_2\text{H}]$ ( $10^{-2}\text{M}$ )	—	—	—	—	—	14.0	14.0	14.0	14.0	14.0
$10k$ ( $\text{mole}^{-1} \text{sec.}^{-1}$ )	1.31	1.46	1.74	2.22	3.19	1.33	1.37	1.45	1.66	1.88

spectroscopically the indicator ratios  $[\text{BH}^+]/[\text{B}]$  for *m*-nitroaniline.<sup>8</sup> The results are given in Tables 7 and 8.

*Infrared Spectroscopy.*—The infrared spectra of trifluoroacetic and benzoic acid alone and in admixture in carbon tetrachloride were recorded in the C=O stretching region (Fig. 3). While

<sup>8</sup> Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., 1940, p. 251; Long and Paul, *Chem. Rev.*, 1957, **57**, 1, 1286.

TABLE 7.

Indicator ratio in carbon tetrachloride at 25° (B = *m*-nitroaniline, 1 × 10<sup>-2</sup> g./l.).

Exp. no. ....	1	2	3	4	5	6	7	8	9	10	11
[CF <sub>3</sub> ·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	1.02	2.56	5.13	2.62	5.25	0.94	2.38	4.77	0.94	2.38	4.77
[Ph·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	—	—	—	2.55	2.55	1.0	1.0	1.0	6.0	6.0	6.0
BH <sup>+</sup> /B .....	0.12	1.1	4.1	0.20	1.40	0.07	0.52	2.54	0.05	0.13	0.56

TABLE 8.

Indicator ratio in benzene at 25° (B = *m*-nitroaniline, 1 × 10<sup>-2</sup> g./l.).

Exp. no. ....	12	13	14	15	16	17	18	19	20	21
[CF <sub>3</sub> ·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	1.33	2.36	3.80	7.76	1.33	3.80	7.76	1.33	3.80	7.76
[Ph·CO <sub>2</sub> H] (10 <sup>-2</sup> M) .....	—	—	—	—	1.0	1.0	1.0	10.0	10.0	10.0
BH <sup>+</sup> /B .....	0.2	0.48	0.90	3.5	0.15	0.7	3.0	0.1	0.35	1.22

the spectrum of each acid shows the familiar bands for the free and the associated acid at the usual frequencies, the spectra of the mixed acids are much more complex and indicate mixed association of the acids.

## DISCUSSION

Acid catalysis in the oxidation of a sulphide (and, in general, of any nucleophile) with a hydroperoxide, according to reaction (1) results from an equilibrium, as shown in (3) where the protonated peroxide is a stronger electrophile than its conjugate base:



The concentration of the protonated species will depend on the concentration of the protonating acid and on the basicity of the peroxide. When R = H or alkyl (hydrogen peroxide or an alkyl hydroperoxide), the oxidation is very sensitive to acid-catalysis; when R = acyl then, because of the low basicity of peroxyacid, the catalysis is negligible except at very high acidity.<sup>1-3,5-7</sup> In line with this, we found that trifluoroacetic but not benzoic acid, catalyzes the oxidation of aryl sulphides by peroxybenzoic acid.

The catalysis is strongly solvent-dependent, and is affected by the presence of weak acids such as benzoic acid.

Trifluoroacetic acid is catalytic in carbon tetrachloride and somewhat less so in benzene, but it has no catalytic effect when the solvent is dioxan or dioxan-water. In dioxan-water, perchloric acid has a weak but definite catalytic effect.\* The catalyzed reaction is slowed by benzoic acid [as shown in runs 20—23 (Table 3) and 38—46 (Table 6), when the concentration of trifluoroacetic acid is held constant and varying amounts of benzoic acid are added]. As benzoic acid is produced during the reaction, the rate of reaction falls as the reaction proceeds, and the system shows complex kinetics. If initial rates are taken, however, the velocity of the oxidation shows a linear dependence on the trifluoroacetic acid concentration (Tables 2, 4, and 6; Fig. 1), following equation (4):

$$\text{Rate} = k[\text{R}_2\text{S}][\text{Ph}\cdot\text{CO}_3\text{H}] + k'[\text{R}_2\text{S}][\text{Ph}\cdot\text{CO}_3\text{H}][\text{CF}_3\cdot\text{CO}_2\text{H}]. \quad (4)$$

When a large excess of benzoic acid is present initially, so that its concentration is essentially constant during the run, the reaction follows clean second-order kinetics (Fig. 1), as described by equation (4). The velocity is a linear function of the trifluoroacetic acid concentration, but the catalytic constant *k'* is much smaller.

These results can be interpreted if it is assumed that the effective acidity of trifluoroacetic acid, *i.e.*, ability to protonate peroxybenzoic acid, is dependent on both the solvent and the presence of benzoic acid.

\* Unpublished results: the catalyzed oxidation of *p*-nitrodiphenyl sulphide (HClO<sub>4</sub>: 2 × 10<sup>-2</sup>M) has a reaction coefficient (*k*, sec.<sup>-1</sup> mole<sup>-1</sup> l.) of 0.65, while for the uncatalyzed reaction *k* = 0.5, both in dioxan-water (50 : 50) at 25°; in this solvent, trifluoroacetic acid does not appreciably increase the rate up to 0.25M-concentration.

This effective acidity has been determined in the various systems by measuring the indicator ratio  $[\text{BH}^+]/[\text{B}]$  for the base *m*-nitroaniline (Tables 7 and 8). At a constant concentration of trifluoroacetic acid, the effective acidity is lower in benzene than in carbon tetrachloride; and in both solvents the addition of benzoic acid strongly depresses the acidity. There is thus a strict correlation between acidity as measured by  $[\text{BH}^+]/[\text{B}]$  and catalytic activity, and it seems justified to assume that the two phenomena have a common origin.

It is known<sup>9</sup> that carboxylic acids are largely associated in these solvents, as dimers or polymers. Two or more carboxylic acids should give mixed association, and the infrared spectra of benzoic and trifluoroacetic acid in carbon tetrachloride (Fig. 3) show that this does occur, although the spectra are too complex to allow detailed analysis.<sup>10</sup>

In our case then (we consider only dimers, for simplicity), the monomeric benzoic and trifluoroacetic acid will be in equilibrium with the dimeric species  $(\text{CF}_3\cdot\text{CO}_2\text{H})_2$ ,  $(\text{Ph}\cdot\text{CO}_2\text{H})_2$ , and  $(\text{Ph}\cdot\text{CO}_2\text{H}, \text{CF}_3\cdot\text{CO}_2\text{H})$ . As the basicity of benzoic acid is relatively high it reduces the ability of the trifluoroacetic acid bound to it to protonate or associate with the peroxybenzoic acid. This mixed "dimer" seems to be quite stable, as the addition of an equimolar amount of benzoic acid strongly depresses both the catalysis and the apparent acidity measured by the indicator ratio.

A similar effect has recently been reported by Andrews and Keefer<sup>10</sup> in the inhibition by acetic acid of trifluoroacetic acid-catalyzed halogenation and related reactions. On the other hand, Berti *et al.*<sup>7</sup> suggested that a reaction similar to that studied here (epoxidation of olefins in benzene by peroxybenzoic acid catalyzed by trichloroacetic acid) follows a kinetic equation of the type (5):

$$\text{Rate} = k[\text{C}=\text{C}][\text{Ph}\cdot\text{CO}_2\text{H}][\text{CCl}_3\cdot\text{CO}_2\text{H}]^{1/2}. \quad (5)$$

If the inhibition of catalysis is a general effect, as it seems to be, the different rate equation found by these authors might be due to the fact that the above factors (and possibly the uncatalyzed rate of reaction) were not taken into consideration.

#### EXPERIMENTAL

*Reagents.*—*p*-Nitrodiphenyl sulphide<sup>11</sup> and *pp'*-dinitrodiphenyl sulphide<sup>12</sup> were obtained by published methods.

The peroxybenzoic acid<sup>13</sup> was crystallized from pentane; <sup>2,3c</sup> iodometric analysis showed the peracid content to be 80—90% in different samples. The only impurity was benzoic acid.

"Anala.R" trifluoroacetic acid was purified by distillation, and *m*-nitroaniline and benzoic acid by recrystallization from water.

"Anala.R" carbon tetrachloride, benzene, and dioxan were purified by usual methods<sup>14</sup> and fractionally distilled.

*Reaction Products.*—Equimolecular amounts of peroxybenzoic acid and sulphide in benzene or carbon tetrachloride, with or without trifluoroacetic acid, were made to react to completion at room temperature. The solution was then washed with 10% aqueous sodium carbonate and dried under a vacuum. Acidification of the alkaline solution and extraction with chloroform gave an almost quantitative yield of benzoic acid. The residue obtained on evaporation of the solvent, when analyzed by infrared spectroscopy, appeared to contain sulphoxide (80—90%), as well as sulphide and sulphone (5—10%).

*Kinetic Method.*—The reactions were followed by the consumption of peroxybenzoic acid,

<sup>9</sup> Bell and Arnold, *J.*, 1934, 1969; Harris and Hobbs, *J. Amer. Chem. Soc.*, 1954, **76**, 1419; Reews, *Canad. J. Chem.*, 1961, **39**, 1711; Parmigiani, Perotti, and Riganti, *Gazzetta*, 1961, **91**, 1148.

<sup>10</sup> For analogous results see Andrews and Keefer, *J. Amer. Chem. Soc.*, 1960, **82**, 4547; see also *ibid.*, 1961, **83**, 376.

<sup>11</sup> Willgerodt and Klinger, *J. prakt. Chem.*, 1912, **85**, 189; Mangini and Passerini, *J.*, 1956, 4954.

<sup>12</sup> Waldron and Reid, *J. Amer. Chem. Soc.*, 1923, **45**, 2399; Mangini and Passerini, *ref. 11*.

<sup>13</sup> Kergomard and Bigou, *Bull. Soc. chim. France*, 1956, 486.

<sup>14</sup> Weissberger, "Technique of Organic Chemistry," Vol. VII, "Organic Solvents," Interscience Publ. Inc., New York, 1955.

as previously described,<sup>3</sup> and the rate coefficients were calculated graphically; initial rates were evaluated when necessary (see text and Tables). The  $k$  values calculated from different runs at constant concentration of trifluoroacetic and benzoic acid did not usually differ by more than 2—3%; a larger error (~5%) is estimated for the fastest runs.

Typical runs are shown in Fig. 2; other numerical data are given in Table 9.

TABLE 9.  
Typical runs.

$(p\text{-NO}_2\text{-C}_6\text{H}_4)_2\text{S } 0\cdot01778\text{M}; \text{Ph}\cdot\text{CO}_2\text{H } 0\cdot01427\text{M}; \text{in } \text{C}_6\text{H}_6 \text{ at } 13\cdot0^\circ.$											
5-ml. samples titrated with $0\cdot01937\text{N-Na}_2\text{S}_2\text{O}_3$ .											
Time (sec.) .....	0	33	60	90	120	150	180	225	328	394	540
Titre (ml.) .....	7·37	6·85	6·47	6·08	5·73	5·42	5·17	4·73	4·06	3·67	3·02
$10k$ (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	—	1·23	1·26	1·28	1·29	1·29	1·27	1·31	1·29	1·31	1·30

$(p\text{-NO}_2\text{-C}_6\text{H}_4)_2\text{S } 0\cdot01758\text{M}; \text{Ph}\cdot\text{CO}_2\text{H } 0\cdot01442\text{M}; \text{CF}_3\cdot\text{CO}_2\text{H } 0\cdot01814\text{M}; \text{Ph}\cdot\text{CO}_2\text{H } 0\cdot1404\text{M}; \text{in } \text{C}_6\text{H}_6 \text{ at } 13\cdot0^\circ.$											
5-ml. samples titrated with $0\cdot01968\text{N-Na}_2\text{S}_2\text{O}_3$ .											
Time (sec.) .....	0	38	51	65	82	100	129	153	184	207	255
Titre (ml.) .....	7·34	6·70	6·50	6·30	6·05	5·81	5·48	5·22	4·92	4·71	4·31
$10k$ (mole <sup>-1</sup> sec. <sup>-1</sup> l.) .....	—	1·42	1·43	1·44	1·45	1·46	1·45	1·46	1·45	1·46	1·48

$(p\text{-NO}_2\text{-C}_6\text{H}_4)_2\text{S } 10\cdot01758\text{M}; \text{Ph}\cdot\text{CO}_2\text{H } 0\cdot01442\text{M}; \text{CF}_3\cdot\text{CO}_2\text{H } 0\cdot03628\text{M}; \text{in } \text{C}_6\text{H}_6 \text{ at } 13\cdot0^\circ.$											
5-ml. samples titrated with $0\cdot01968\text{N-Na}_2\text{S}_2\text{O}_3$ .											
Time (sec.) .....	0	20	34	48	62	80	118	183	302		
Titre (ml.) .....	7·34	6·80	6·58	6·32	6·12	5·86	5·38	4·74	4·20		
$10k$ (mole <sup>-1</sup> sec. <sup>-1</sup> l.) ...	—	2·22	1·91	1·88	1·79	1·75	1·70	1·62	1·39		

*Infrared Spectra.*—Infrared spectra in carbon tetrachloride solution were recorded with a 0·1-mm. cell in a Beckman IR4 instrument fitted with a sodium chloride prism.

*Indicator Measurements.*—The measurements on *m*-nitroaniline were carried out with a Beckman DU instrument in the region 340—360  $\mu$ .

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