The Oxidation of Olefins with Perbenzoic Acids. A Kinetic Study.

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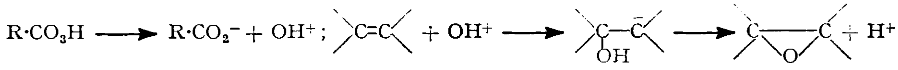
The rates of epoxidation of various olefins with substituted perbenzoic acids have been measured at four temperatures, and the entropies, free energies, and heats of activation have been calculated. A theory is advanced for the mechanism of the reaction.

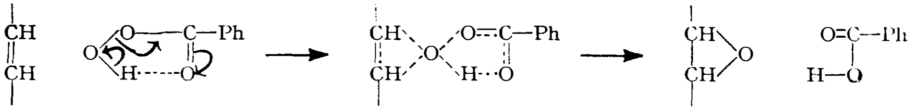
Per-acid oxidation of olefins in non-polar solvents gives excellent yields of the corresponding epoxides (cf. Swern, " Organic Reactions," Wiley, 1953, Vol. VII, p. 378), and has been shown (cf. Boeseken and Blumberger, *Rec. Trav. chim.*, 1925, **44**, 90; Boeseken and Stuurman, *ibid.*, 1937, **56**, 1034; Medvedev and Blokh, *J. Phys. Chem. U.S.S.R.*, 1933, **4**, 721) to be of the first order with respect to both olefin and per-acid. Since the relative reaction velocities of various olefins indicate that the per-acids are electrophilic reagents (Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692), it has been suggested that the per-acids act by the provision of free hydroxyl cations (Robertson and Waters, *J.*, 1948, 1574; Weisenborn and Taub, *J. Amer. Chem. Soc.*, 1952, **74**, 1329), *i.e.* :



However, epoxidation always results in *cis*-addition (see, *e.g.*, Braun, *ibid.*, 1929, **51**, 228; Witnauer and Swern, *ibid.*, 1950, **72**, 3364; King, *J.*, 1942, 387; Atherton and Hilditch, *J.*, 1943, 204), thus precluding formation of a free carbonium ion (unless the life of the ion is less than the period of rotation about a single bond). Waters (Gilman, " Organic Chemistry," Wiley, New York, 1953, Vol. IV, p. 1165) has stated that, since epoxidation is a bimolecular process, the hydroxyl cation cannot become a free entity, and has proposed a modified mechanism which is analogous to that of the addition of halogens to olefins.

Swern (*op. cit.*, p. 386) has suggested a mechanism involving acid-catalysis, giving a transition state which is reminiscent of that for the acid-catalysed fission of epoxides (cf. Hammett, " Physical Organic Chemistry," McGraw-Hill, 1940, Chapter VI).

The present paper reports the rates of epoxidation of various olefins by substituted perbenzoic acids in benzene and diethyl ether solutions, with the object of extending to epoxidation the molecular mechanisms recently proposed for the mode of action of perbenzoic acid on substituted benzaldehyde phenylhydrazones (Lynch and Pausacker, *J.*, 1954, 1131), 4 : 4′-dichlorodibenzyl sulphide (Overberger and Cummins, *J. Amer. Chem. Soc.*, 1953, **75**, 4250), and diphenyl sulphoxide (Szmant, Harnsberger, and Krahe, *ibid.*, 1954, **76**, 2185), *i.e.* :



(Cf. Bartlett, *Record Chem. Progr.*, 1950, **11**, 51.)

EXPERIMENTAL

M. p.s are corrected. " Peroxide " oxygen was determined by iodometric titration (see below). Other analyses were performed under the direction of Dr. K. W. Zimmermann.

Reagents.—Substituted perbenzoic acids were prepared by Braun's method (*Org. Synth.*, Coll. Vol. I, 1946, p. 431) as modified by Kolthoff, Lee, and Mairs (*J. Polymer Sci.*, 1947, **2**, 199) and Overberger and Cummins (*loc. cit.*). M. p.s, yields, and analyses are given in the following Table. M. p.s in parentheses are those reported in the literature.

			" Peroxide " oxygen	
Substituent	M. p.	Yield (%)	Found (%)	Required (%)
4-OMe	86° (86°)	60	9·2	9·5
4-Me	95 (95)	93	10·4	10·5
Nil	40 (41)	94	10·9	11·6
4-Cl	108 (111)	32	9·3	9·3
3-Cl	88	66	9·4	9·3
3-NO_2	101	66	8·5	8·7
4-NO_2	136 (134)	42	8·7	8·7

Diethyl ether was purified by Vogel's method (" A Textbook of Practical Organic Chemistry," Longmans, 1950, p. 162).

Benzene was purified by Vogel's method (*op. cit.*, p. 171) and dried over sodium.

Magnesium perchlorate (B.D.H. " Anhydrous ") was dried at 110° for 4 hr. immediately before use.

Benzoic acid was recrystallised from ethanol and had m. p. 122°.

Monosubstituted *trans*-stilbenes were prepared by the Meerwein reaction (cf. Meerwein, Buchner, and Emster, *J. pr. Chem.*, 1939, **152**, 237). *trans*-4 : 4′-Dimethoxystilbene was obtained by reduction of *p*-anisaldehyde with alkaline ethylene glycol (Tadros, Ekladius, and Sakla, *J.*, 1954, 2351). The *trans*-stilbenes were crystallised from ethanol immediately before use. Their m. p.s are given in the following Table.

Substituent	4-OMe	3-Me	4-Me	Nil	3-Cl
M. p.	134° (135°)	52° (53°)	118° (117°)	123° (123°)	73° (73°)
Substituent	4-Cl	3-NO_2 *	4-NO_2	4 : 4′-$(OMe)_2$	
M. p.	130° (129°)	113°	157° (155°)	214° (214°)	

* Found : C, 75·1 ; H, 4·9 ; N, 6·2. $C_{14}H_{11}O_2N$ requires C, 74·7 ; H, 4·9 ; N, 6·2%.

Styrene was twice distilled immediately before use (b. p. 146°).

cis-Stilbene, b. p. 140°/10 mm., was prepared by Taylor and Crawford's method (*J.*, 1934, 1130).

Triphenylethylene was prepared by Adkins and Zartman's procedure (*Org. Synth.*, 1937, **17**, 89) and after crystallisation from ethanol had m. p. 71° (lit., 72°).

Tetraphenylethylene, m. p. 224° (lit., 223—224°) was prepared by reduction from benzophenone *via* benzpinacol and benzpinacolone (cf. Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 449), and was crystallised from benzene–ethanol.

*cyclo*Hexene, b. p. 83°, was purified by Waterman and van Westen's method (*Rec. Trav. chim.*, 1929, **48**, 637).

Apparatus.—A bath was used whose temperature was controlled to within ±0·05°. Reactions were performed in calibrated standard 50-ml. flasks. Blackened flasks were used for the reactions with *cis*-stilbene.

Yields of Products.—The appropriate olefin (*ca.* 2·5 × 10^{-2} mole) was added to a solution of perbenzoic acid (*ca.* 2·8 × 10^{-2} mole) in benzene (100 ml.), and the mixture was kept at 30° for 4 days. Residual acids were removed by extraction with sodium hydrogen carbonate, and the solvent was evaporated under reduced pressure. The residues were purified by crystallisation (from ethanol) or distillation. Yields, etc., of the epoxides are listed in the Tables.

(a) trans-*Stilbene epoxides.*

Substituent	4 : 4′-$(OMe)_2$	4-OMe	4-Me	3-Me [a]	Nil
M. p.	142° (142°)	119° (118°)	61° (59°)	66°	68° (69°)
Yield (%)	98	95	99	99	100
Substituent	3-Cl [b]	4-Cl [c]	3-NO_2 [d]	4-NO_2	
M. p.	60°	100°	81°	125° (125°)	
Yield (%)	95	96	98	96	

[a] Found: C, 85·8; H, 7·0. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%. [b] Found: C, 72·6; H, 5·3; Cl, 15·3. $C_{14}H_{11}OCl$ requires C, 72·9; H, 4·8; Cl, 15·4%. [c] Found: C, 72·8; H, 4·6; Cl, 15·2%. [d] Found: C, 69·4; H, 4·5; N, 6·2. $C_{14}H_{11}O_3N$ requires C, 69·7; H, 4·6; N, 5·8%.

(b) *Other epoxides.*

Epoxide	Styrene	*cis*-Stilbene	CHPh:CPh_2	CPh_2:CPh_2	*cyclo*Hexene
M. p./B. p.*	101°/40 mm.*	43° (42°)	78° (75—77°)	200° (201°)	132° *
Yield (%)	80	85	88	100	100

* Denotes b. p.

Method of Estimation.—The olefin (*ca.* 2—3 × 10^{-3} mole) was weighed into the reaction vessel, which was placed in the bath until temperature equilibrium was attained. A pre-heated solution of the appropriate perbenzoic acid (*ca.* 6—8 × 10^{-2}M) was added to the mark, and the mixture was shaken vigorously. Aliquot portions (5 ml.) were withdrawn at determined times and added to 0·5N-potassium iodide (5 ml.) and 2N-sulphuric acid (10 ml.). The liberated iodine was titrated with 0·08N-sodium thiosulphate (starch). The perbenzoic acids were also estimated in this way. When diethyl ether was used as solvent, it was necessary to add carbon tetrachloride to the titration mixture in order to obtain satisfactory end-points (cf. Lynch and Pausacker, *loc. cit.*).

Results.—Reactions were followed in the range 0—60% completion, and were found to obey second-order kinetics. The rate constants, calculated by standard methods, obeyed the Arrhenius equation.

The reaction of *trans*-stilbene with perbenzoic acid in benzene at 30° is given as a typical example in Table 1.

TABLE 1.

Initial olefin concn. = 0·04932M (7·00 ml. of 0·07043N-$Na_2S_2O_3$)
Initial perbenzoic acid concn. = 0·06416M (9·11 ml. of 0·07043N-$Na_2S_2O_3$)
First perbenzoic acid estimation = 8·94 ml.
Equiv. olefin concn. = 6·83 ml.

Time (min.)	12·0	36·3	70·8	106·0	155·0	216·5	303·0
Titre (ml.)	8·86	8·69	8·48	8·27	7·99	7·64	7·28
10^4k_2 (mole^{-1} l. sec.$^{-1}$)	2·59	2·75	2·68	2·69	2·71	2·74	2·71

Mean : k_2 = 2·70 × 10^{-4} mole^{-1} l. sec.$^{-1}$.

Results obtained at different temperatures are :

Temp.	20°	25°	30°	35°
10^4k_2 (mole^{-1} l. sec.$^{-1}$)	2·69, 2·70	4·25, 4·29	6·56, 6·72	10·2, 10·1

The bimolecular constants obey the Arrhenius equation, as shown by the following data (the calculated values are given by $k = 1·78 \times 10^8 e^{-15,850/RT}$) :

Temp.		20°	25°	30°	35°
10^4k_2:	obs.	2·69$_5$	4·27	6·64	10·1$_5$
	calc.	2·70	4·28	6·68	10·3

(a) *Reactions in benzene.* The results obtained with the various olefins and perbenzoic acids in benzene are summarised in Table 2, duplicates being shown. $\Delta F^{\ddagger}$ and $\Delta H^{\ddagger}$ are in kcal. and $\Delta S^{\ddagger}$ in cal. deg.$^{-1}$. $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ for the various reactions are calculated from the rates at 30°.

TABLE 2. *Oxidation of olefins with substituted perbenzoic acids.*

(i) trans-*Stilbenes and perbenzoic acids.*

Substituted stilbene	Substituted perbenzoic acid	10^4k (mole^{-1} l. sec.$^{-1}$)					$\Delta H^{\ddagger}$	$\Delta F^{\ddagger}$	$-\Delta S^{\ddagger}$
		20°	25°	30°	35°	40°			
4 : 4′-(OMe)$_2$	Nil	—	83·6 83·0	128 128	180 182	270 277	14·0	20·4	21·1
4-OMe	Nil	13·0 13·2	20·2 20·2	31·2 31·5	48·0 48·0	—	14·5	21·2	22·3
4-Me	Nil	6·17 6·17	9·72 9·64	15·0 14·7	22·5 23·2	—	15·0	21·7	22·2
3-Me	Nil	3·07 3·03	4·80 4·85	7·41 7·50	11·3 11·8	—	15·2	22·1	22·7
Nil	Nil	2·69 2·70	4·25 4·29	6·72 6·56	10·2 10·1	—	15·2$_5$	22·2	22·8
4-Cl	Nil	1·70 1·72	2·68 2·70	4·22 4·33	6·53 6·56	—	15·6	22·4$_5$	22·6
3-Cl	Nil	1·04 1·07	1·74 1·79	2·73 2·79	4·25 4·31	—	15·9$_5$	22·7	22·2
3-NO$_2$	Nil	—	0·70 0·75	1·12 1·16	1·70 1·70	2·68 2·63	16·4	23·2$_5$	22·6
4-NO$_2$	Nil	--	0·62 0·64	0·98 0·97	1·51 1·60	2·30 2·50	16·6$_5$	23·3	22·0
Nil	4-NO$_2$	29·5 29·0	44·4 44·0	66·8 66·2	97·5 98·0	—	13·8	20·8	23·1
4-NO$_2$	4-NO$_2$	3·40 3·40	5·31 5·41	8·25 8·28	12·4 12·5	—	15·1	22·0	22·7
Nil	3-NO$_2$	26·4 27·1	39·2 39·7	58·9 59·0	89·0 89·0	—	13·9	20·8$_5$	23·0
Nil	3-Cl	9·90 9·95	15·0 15·0	23·1 23·5	34·2 33·7	—	14·5$_5$	21·4	22·9
Nil	4-Cl	6·51 6·80	10·2 10·5	15·1 16·0	24·6 23·6	—	14·9	21·6$_5$	22·4
Nil	4-Me	—	2·39 2·37	3·73 3·78	5·63 5·66	8·41 8·58	15·6	22·5	22·9
Nil	4-OMe	0·81 0·82	1·30 1·35	2·12 2·20	3·40 3·50	—	16·0$_5$	23·0	22·8

(ii) *Other olefins and perbenzoic acid.*

Olefin	10^4k (mole^{-1} l. sec.$^{-1}$)					$\Delta H^{\ddagger}$	$\Delta F^{\ddagger}$	$-\Delta S^{\ddagger}$
	20°	25°	30°	35°	40°			
Styrene	6·12 6·20	9·64 9·65	14·0 14·4	21·2 21·4	—	14·2	21·7	24·8
cis-Stilbene	5·70 5·80	8·96 8·74	13·0 13·7	19·6 19·7	—	14·1	21·7$_5$	25·2
Triphenylethylene ...	—	2·05 2·06	3·07 3·08	5·02 5·00	7·01 7·40	15·7	22·6	22·7
Tetraphenylethylene	—	—	0·27 0·29	0·45 0·43	0·79 0·79	17·2	24·1	22·6
*cyclo*Hexene	127 127	180 182	264 263	360 365	—	12·7	19·9$_5$	24·0

(b) *Reactions in diethyl ether.* Only the reactions of *trans*-stilbene and *cyclo*hexene with perbenzoic acid were investigated in ether. The reactions were of second order and the rates of reaction obeyed the Arrhenius equation. Summarised results (units as before) are :

Olefin	10^4k (mole^{-1} l. sec.$^{-1}$)					$\Delta H^{\ddagger}$	$\Delta F^{\ddagger}$	$-\Delta S^{\ddagger}$
	15°	20°	25°	28°	30° (calc.)			
trans-Stilbene	0·17 0·16	0·29 0·30	0·50 0·51	0·67 0·67	0·84	17·9	23·4	18·2
*cyclo*Hexene	2·25 2·20	3·72 3·75	5·82 5·85	7·50 7·50	8·96	15·3	22·0	22·0

(c) *Acid-catalysis and salt effects.* The effect of added benzoic acid on the oxidation rate of *trans*-stilbene with perbenzoic acid in benzene was investigated at 30°. For a mixture containing *trans*-stilbene ($5{\cdot}8 \times 10^{-2}$M) and perbenzoic acid ($6{\cdot}4 \times 10^{-2}$M), the following rates were observed in the presence of varying concentrations of benzoic acid :

Acid concn. (10^2M)	1·4	2·9	6·6	8·1
10^4k (mole^{-1} l. sec.$^{-1}$)	6·65	6·58	6·57	6·68

The effect of added salt on the oxidation rates of *trans*-stilbene and *cyclo*hexene by perbenzoic acid in diethyl ether at 25° was investigated by addition of magnesium perchlorate. Results were :

Olefin	Olefin concn. (M)	Peracid concn. (M)	$Mg(ClO_4)_2$ concn. (M)	10^4k (mole^{-1} l. sec.$^{-1}$)
trans-Stilbene	0·11	0·17	0·01	0·51, 0·51
*cyclo*Hexene	0·05	0·08	0·013	5·71, 6·07

DISCUSSION

The entropy of activation is virtually constant for the reactions of *trans*-stilbenes with perbenzoic acids in benzene solution, so either the free energies of activation or the heats of activation may be used to interpret the effects of substituents on the electron density at the reacting centres, as differences in these quantities are then both equal to the potential-energy change for the reaction (Hammett, *op. cit.*, pp. 118 *et seq.*). Examination of the effects of the various substituents in these reactions shows that, although there are not very large changes in the free energies and heats of activation, electron-donating substituents in *trans*-stilbene decrease these quantities, whereas electron-accepting substituents increase them. With the substituted perbenzoic acids, however, electron-accepting substituents decrease, and electron-donating substituents increase, the free energies and heats of activation. The effect of substituents is more apparent when the rates (10^4k at 30°) are listed : (*a*) substituted *trans*-stilbenes with perbenzoic acid, 4 : 4′-$(OMe)_2$ (128) > 4-OMe (31·3) > 4-Me (14·8) > 3-Me (7·45) > Nil (6·64) > 4-Cl (4·22) > 3-Cl (2·76) > 3-NO_2 (1·14) > 4-NO_2 (0·98); (*b*) substituted perbenzoic acids with *trans*-stilbene, 4-NO_2 (66·5) > 3-NO_2 (59·0) > 3-Cl (23·3) > 4-Cl (15·5) > Nil (6·64) > 4-Me (3·75) > 4-OMe (2·16). The qualitative effects of substituents are therefore in accord with the characters of olefins and per-acids as nucleophilic and electrophilic reagents respectively (cf. Swern, *loc. cit.*).

Further, there are satisfactory linear relations between the logarithms of the rate constants (at 30°) and Hammett's "sigma" constant for the substituent (Hammett, *op. cit.*, pp. 184 *et seq.*), for the series of substituted *trans*-stilbenes and perbenzoic acids, and these are shown in Figs. 1 and 2. The methoxy-substituted compounds show the greatest divergences, which is not unusual (cf. Jaffé, *Chem. Rev.*, 1953, **53**, 191).

Comparison of the rates of epoxidation of *trans*-stilbene and of *cyclo*hexene by perbenzoic acid in diethyl ether and in benzene shows that the rates are much greater in benzene, with lower free energies and heats of activation. This would not be expected if the reaction is ionic, since the more polar diethyl ether would be expected to increase the rates and decrease the activation energies. The effect of solvent in this reaction is similar to that observed in the per-acid oxidation of phenylhydrazones (Lynch and Pausacker, *loc. cit.*) and alkyl sulphides (Overberger and Cummins, *loc. cit.*), but is in contrast to that in the per-acid oxidation of ketones where the rates increase with increasing polarity of the solvent (Friess and Pinson, *J. Amer. Chem. Soc.*, 1952, **74**, 1302).

Addition of magnesium perchlorate did not affect the oxidation rates of *trans*-stilbene or of *cyclo*hexene by perbenzoic acid in diethyl ether at 25°. This is consistent with the proposed mechanism of epoxidation, since the transition state is non-ionic, but eliminates any process involving ionisation of the per-acid as a rate-determining step.

Similarly, it was found that addition of benzoic acid to the oxidation mixture of *trans*-stilbene and perbenzoic acid in benzene at 30° did not affect the rate of oxidation within experimental error. This is in contrast to Swern's assertion (*op. cit.*, p. 385) that "per-acid oxidations so far investigated are subject to general acid-catalysis," although Boeseken and Stuurman (*loc. cit.*) and Medvedev and Blokh (*loc. cit.*) found that oxidations of olefins by peracetic acid in acetic acid, and by perbenzoic acid in xylene, were not acid-catalysed.

The observed second-order kinetics in all the reactions studied shows, furthermore, that the benzoic acid formed as a reaction product does not catalyse the reaction. However, it has been shown (Friess, *J. Amer. Chem. Soc.*, 1949, **71**, 2571; Friess and Soloway, *ibid.*, 1951, **73**, 3968) that the reactions of per-acids with ketones are acid-catalysed, as with many other addition reactions of carbonyl compounds. Swern has drawn his examples of acid-catalysed per-acid oxidations from this class of reaction, but they are not relevant to the mechanism of epoxidation.

The reactivity towards perbenzoic acid of the series of phenyl-substituted ethylenes follows the double-bond orders of the olefinic links (*i.e.*, styrene > *trans*-stilbene > triphenylethylene > tetraphenylethylene) as calculated by Coulson and Jacobs (*J.*, 1949, 2805). In epoxidation, therefore, it may be postulated that perbenzoic acid acts as a "double-bond reagent" (Badger, *Quart. Rev.*, 1951, **5**, 147), *i.e.*, that reaction involves attack on the olefinic bond and not on one of the constituting carbon atoms. Support for this is furnished by the virtual identity of the rates of epoxidation of 2-methylpropene and but-2-ene by peracetic acid in acetic acid solution (Boeseken and Stuurman, *loc. cit.*).

FIG. 1. *Relation between the rate constant at 30° and the Hammett "sigma" constant for reaction of perbenzoic acid with substituted* trans-*stilbenes.*

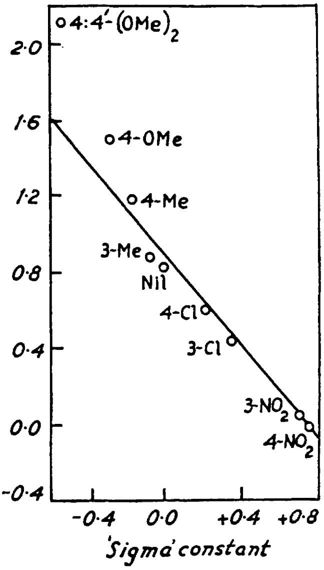
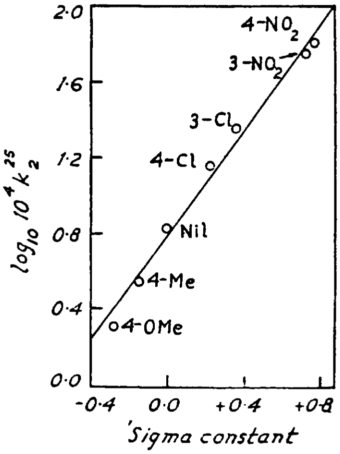
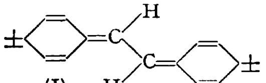
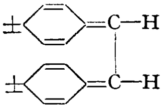


FIG. 2. *Relation between the rate constant at 30° and the Hammett "sigma" constant for reaction of* trans-*stilbene with substituted perbenzoic acids.*



The structure of *trans*-stilbene has been determined by *X*-ray methods (Robertson, Prasad, and Woodward, *Proc. Roy. Soc.*, 1936, *A*, **154**, 187; Robertson and Woodward, *ibid.*, 1937, *A*, **162**, 568; *J.*, 1936, 1817), which show that the molecule is planar. Owing to contributions of structure (I) to the resonance hybrid, the olefinic bond will have some single-bond character, so that the electron density at this bond will be below that expected in the absence of conjugation. With *cis*-stilbene, however, scale models and scale diagrams show that the two rings cannot be coplanar. This will suppress the conjugation, so that structures of type (II) can make no appreciable contribution to the normal state of the molecule. The electron density around the olefinic link will therefore be much greater than that in the *trans*-compound (cf. *cis*- and *trans*-azobenzene; Badger, Buttery, and Lewis, *J.*, 1953, 2145). It would be expected, therefore, that *cis*-stilbene would be


(I)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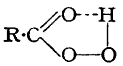
(III)

epoxidised more rapidly than *trans*-stilbene, and this is confirmed by the results shown in Table 2. The free energy and the heat of activation are lower for *cis*-stilbene, which is epoxidised at almost the same rate as styrene.

The proposed mechanism is further supported by recent investigations of the infra-red absorption spectra of the organic per-acids. Measurements by Davison (*J.*, 1951, 2456), Giguere and Olmos (*Canad. J. Chem.*, 1952, **30**, 821), and Minkoff (*Proc. Roy. Soc.*, 1954, *A*, **224**, 176) show that per-acids exist in solution very largely in the monomeric, intramolecularly hydrogen-bonded form (III). The increased volatility of the per-acids compared with the corresponding carboxylic acids is probably due to this intramolecular chelation, which renders impossible the characteristic dimerisation noted with the carboxylic acids.

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