Calorimetric, 1H Nuclear Magnetic Resonance, and Molecular Orbital Studies of Hydrogen Bonding between Peroxy Acids and Oxygen Bases. Implications for Mono-oxygen Donation Potential of Peroxy Acids

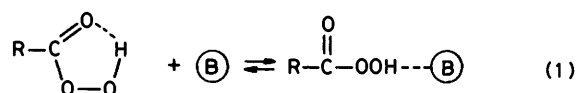Božo Plesničar,* Viktor Menart, Milan Hodošček, Jože Koller,* Franci Kovač, and Jože Škerjanc*
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The enthalpies of formation of hydrogen-bonded complexes between peroxybenzoic acids and various oxygen bases, $\Delta H°$, were obtained by calorimetry. The 1H n.m.r. shifts of the OOH absorptions, under conditions of complete peroxy acid complexation, were measured. $\Delta H°$ and 'hydrogen-bond shifts', $\Delta\delta OOH = \delta OOH(base) - \delta OOH(CCl_4)$, were found to be sensitive to the acidity of the peroxy acid as well as the basicity of the oxygen base. A satisfactory linear correlation between $\Delta H°$ and $\Delta\delta OOH$, expressed by the equation $-\Delta H°(kJ\ mol^{-1}) = (7.59 \pm 0.92)\Delta\delta OOH + (7.35 \pm 1.61)$, was found. Ab initio MO SCF calculations (STO-4G, 4-31G*) were carried out for the peroxyformic acid–dimethyl ether complex and peroxyformate ion. The peroxy acid isotope effect for epoxidation of cyclohexene with 4-t-butylperoxybenzoic acid (OH/OD) in NN-dimethylacetamide (k_H/k_D 1.09), together with the results of kinetic studies in other oxygen bases as solvents, suggest that oxygen base is most probably a part of an 'early', loose charge-transfer-type transition state for these reactions ('direct attack mechanism'), and that reduced reactivity of peroxy acids in basic solvents most probably reflects lowered electrophilicity of the peroxy acid due to the forcing of the enlarged negative charge on the terminal oxygen atom after complexation.

The transfer of an oxygen atom from peroxy acids to various substrates is of considerable practical and theoretical interest to both organic[1] and biologically[2] oriented chemists. These reagents were also chosen as possible models for cytochrome P-450-dependent mono-oxygenases based on their ability to hydroxylate alkanes, to epoxidize C=C bonds, and to elicit the NIH shift in the oxidation of aromatic compounds ('oxenoid mechanism').[2a] It has recently been even suggested that peroxy acids may be involved in cytochrome P-450 reactions.[2c]

Oxidations with peroxy acids are among the more complex and least well understood reactions in organic chemistry. In spite of considerable work on the mechanism of this reaction, several fundamental questions remained unanswered.[1] It is thus tempting to investigate various aspects of the structure and reactivity of this important class of oxidants.

Experimental[3-9] and theoretical[10-18] evidence indicates that peroxy acids exist in 'inert' solvents and in the gas phase as intramolecularly hydrogen-bonded chelates. This form has generally been regarded as the 'effective' one in oxidations of various substrates with these reagents. Solvents and systems with basic oxygen are able to disrupt the five-membered peroxycarboxylate ring to form intermolecularly hydrogen-bonded complexes [equation (1)]. Stable crystalline 1:1

$$R-C\underset{O-O}{\overset{\overset{\textstyle O}{\diagup}}{\diagdown}}H + \circledB \rightleftharpoons R-\overset{\overset{\textstyle O}{\|}}{C}-OOH---\circledB \qquad (1)$$

complexes between peroxybenzoic acids and phosphine, arsine, and pyridine oxides have actually been isolated,[19] and the structure of one of them, i.e. the adduct p-nitroperoxybenzoic acid–triphenylphosphine oxide, has been determined by X-ray crystallography.[20]

The above mentioned interactions have a profound influence on the rate of oxidations of various substrates, i.e. olefins,[21-26] acetylenes,[27] and sulphides.[23] However, the nature of the reduced reactivity of peroxy acids, after complexation with the

organic oxygen base, has not yet been clarified unambiguously.

In order to assess quantitatively these interactions, we have undertaken a calorimetric study of the association between peroxybenzoic acids and various oxygen bases. Owing to the great sensitivity of the observed 1H n.m.r. δOOH chemical shifts of peroxy acids to the presence of traces of the parent carboxylic acid and water after complexation with oxygen bases (in dilute CCl_4 solutions), as well as the substantial overlap of broad i.r. νOOH absorptions of peroxy acid complexes with νOOH absorptions of intramolecularly hydrogen-bonded peroxy acids, we were unable to determine reliably and reproducibly the equilibrium constant, K, for complexation [equation (1)] with either of these techniques. Therefore, a 'double reciprocal' ($1/\Delta H$ versus $1/B_o$) analysis of calorimetric data, which proved to be a reliable method for simultaneous determination of equilibrium constants and enthalpies of complex formation, $\Delta H°$, has been used in the present study.[28] Similar analyses of calorimetric data for simultaneous determination of equilibrium constants and enthalpies of complex formation has already been reported in the literature.[29] The 'hydrogen-bond shifts', $\Delta\delta OOH$, i.e. the shift of the completely formed complex relative to uncomplexed peroxy acid, were also measured.

While the experimentaly determined $\Delta H°$ values reflect only overall properties of the interaction between both components of the complex, ab initio MO SCF theories have been extensively used for the prediction of both the geometry and stabilization energy of various hydrogen-bonded adducts.[30] Thus, an ab initio molecular orbital study of hydrogen bonding in peroxyformic acid–dimethyl ether complex has also been undertaken.

Implications of the obtained results on the mono-oxygen donation potential of peroxy acids in epoxidation of olefins were investigated by determining kinetic and activation parameters for the oxidation of cyclohexene with 4-t-butylperoxybenzoic acid and the deuteriated analogue (OH/OD, peroxy acid isotope effect), respectively, in various organic oxygen bases as solvents.

Experimental

Materials.—Carbon tetrachloride was distilled from calcium hydride, stored over a large bed of Linde molecular sieves (4Å), and used within one week of purification. All oxygen bases were obtained from commercial sources and were purified as recommended in standard texts.[31] In addition to the usual procedures for purification, it was necessary to remove traces of olefinic components in tetrahydrofuran, tetrahydropyran, and di-n-butyl ether by treating these ethers with small amounts of bromine.

The purity of all oxygen bases, determined by g.l.c., was never < 99.8%. These purified liquids were used immediately after completion of the purification.

Substituted peroxybenzoic acids were obtained by the procedure of Silbert *et al.*[32] and were purified by repeated crystallization from hexane–diethyl ether mixtures. In all cases, the purity was over 99.7% as determined by iodometry. Peroxybenzoic acids were stored in the dark at $-25\,°C$ and were freshly recrystallized before use. Deuteriated 4-t-butyl-peroxybenzoic acid was obtained by repeated crystallization from CH_3OD. N.m.r. integration indicated over 95 atom % D in the deuteriated peroxy acid.

Nuclear Magnetic Resonance.—N.m.r. spectra were determined at 20 °C with JEOL model JNM-MH-100 spectrometer. The solution concentrations of peroxy acids in organic oxygen bases were calculated from the calorimetric data to give complete complex formation (0.01—0.025M). The chemical shifts were determined relative to the internal standard Me_4Si.

Calorimetry.—Calorimetric measurements were carried out at 25 °C in a commercial LKB 100700-2 batch microcalorimeter with gold reaction cells. Into the larger compartment of the reaction cell 0.02M-peroxy acid in CCl_4 (4.00 ml) was introduced, and into the smaller one base in the same solvent (2.00 ml). The concentration of base was in the range 0.02—0.5M. The reference cell was charged with CCl_4 (4.00 ml) and the same base solution (2.00 ml). Thus the enthalpy of dilution of the base was corrected for. Separate experiments showed the enthalpy of dilution of the peroxy acid to be negligible. No decomposition of peroxy acids under these conditions was detected.

Method of Analysis of Calorimetric Data.—The formation of the 1:1 complex, C, from the acid, A, and the base, B, is represented by the conventional constant, K, defined by equation (2), where square brackets denote the equilibrium

$$K = [C]/[A][B] \qquad (2)$$

concentrations. This equation can also be expressed in terms of the initial concentrations of the acid, A_0, and the base, B_0, in the reaction mixture [equation (3)]. In cases where the base is in

$$K = [C]/\{(A_0 - [C])(B_0 - [C])\} \qquad (3)$$

excess, the following treatment of data can be applied. If the experimentally determined enthalpy of mixing of acid with base, calculated per mole of A which is initially present is ΔH, and that calculated per mole of C which is formed is $\Delta H°$, then $\Delta H°/\Delta H$ [equation (4)] will tend to unity with increasing

$$\Delta H°/\Delta H = A_0/[C] \qquad (4)$$

extent of complex formation. Since we can determine from calorimetric measurements only ΔH, $\Delta H°$ must be determined by an appropriate method. Combination of equations (3) and (4) leads to equation (5). This equation is essentially the same as

$$\frac{1}{\Delta H} = \frac{1}{\Delta H°} + \frac{1}{\Delta H°}\left[\frac{1}{K} + A_0\left(1 - \frac{\Delta H}{\Delta H°}\right)\right]\frac{1}{B_0} \qquad (5)$$

that already reported by Bolles and Drago,[33] although written in another form with another definition of ΔH. If K is known from spectroscopic measurements, then $\Delta H°$ can be calculated directly from equation (5), knowing ΔH for various values of A_0 and B_0.[34] Since we were not able to determine K spectroscopically with a reasonable degree of accuracy, another procedure was needed. Inspection of equation (5) shows that the slope of a plot of $1/\Delta H$ *versus* $1/B_0$ is determined by the expression in the square brackets. If the initial concentration of the acid, A_0, is low enough, the product $A_0(1 - \Delta H/\Delta H°)$, which is always smaller than A_0, becomes negligible in comparison with $1/K$. The plot of $1/\Delta H$ *versus* $1/B_0$ should thus be almost linear. The extrapolation of the curve to $1/B_0 = 0$, where the correction term $A_0(1 - \Delta H/\Delta H°)$ becomes zero, should yield $1/\Delta H°$ as the intercept and $1/(K\Delta H°)$ as the initial slope.

Since such plots are prone to experimental errors (for example, the Lineweaver–Burke plot in enzyme kinetics), the applicability of the method was carefully tested. Excellent agreement with the experimental values for phenol–oxygen base complexes, obtained by other methods,[33,34] was found.

An attempt was made to cover the widest possible range of saturation fraction s (0.25—0.82) [equation (6)] for optimally

$$s = [C]/A_0 \qquad (6)$$

defined K values. The saturation factor s has the limiting values of 0 at $B_0 = 0$ and 1.0 at complete complexation. It has already been pointed out that equilibrium constants are most reliable when they are based on measurements covering as much as possible of the range in s (0.2—0.8), and become rapidly and increasingly uncertain as s approaches 0 or 1.[35]

Kinetics.—The kinetics of epoxidation of cyclohexene was followed by iodometric determination of peroxybenzoic acid according to Friedrich and Fiato.[36] The reaction solutions were analysed until 75% peroxy acid loss was noted. In some cases, it was necessary to correct the observed titres for the decomposition of peroxy acid in the corresponding solvent. Blank tests, however, showed that contribution of spontaneous decomposition of 4-t-butylperoxybenzoic acid to its overall rate consumption was <1% in all cases. Epoxidations were carried out in constant-temperature baths ($\pm0.05\,°C$) in the temperature range 15—30 °C. The kinetic and activation parameters were calculated by the standard methods.[37] The second-order rate constants were invariant over a range of initial reactant concentrations, *i.e.* 0.5—2.5 $\times$ $10^{-2}M$. Cyclohexene oxide was the only product from oxidation in all systems investigated.

Theory

Methods.—All the calculations have been carried out within the closed-shell LCAO-SCF approximation by using three basis sets, *i.e.* the minimal STO-4G [38a] basis set, 4-31G*, which has polarization (*d*-type basis) functions on non-hydrogen atoms,[38b] and 4-31G** which also has *p*-type functions on hydrogen.[38b]

The energy decomposition analysis was performed by the method of Morokuma.[39] The interaction energy, $\Delta E = E_{complex} - E_{monomers}$, was decomposed as in equation (7) where

$$\Delta E = ES + PL + EX + CT + MIX \qquad (7)$$

ES is the electrostatic interaction between the undistorted electron distribution of a monomer A and that of a monomer B,

Table 1. ¹H N.m.r. data for substituted peroxybenzoic acids in various solvents (0.010—0.025M)

X in XC₆H₄CO₃H	pK^a(25 °C) (H₂O)	Carbon tetrachloride $\delta_{OOH}{}^b$	Tetrahydrofuran $\delta_{OOH}{}^c$	$\Delta\delta_{OOH}{}^c$	Tributyl phosphate $\delta_{OOH}{}^c$	$\Delta\delta_{OOH}{}^c$	NN-Dimethylacetamide $\delta_{OOH}{}^c$	$\Delta\delta_{OOH}{}^c$
4-NO₂	7.29	11.63	12.86	1.23	13.38	1.75	14.54	2.91
3-NO₂		11.51	12.97	1.46	13.59	2.08	14.56	3.05
3-Br		11.51	12.85	1.34	13.36	1.85	14.44	2.93
3-Cl	7.60	11.52	12.59	1.07	13.22	1.70	14.38	2.86
4-Cl	7.67	11.59	12.60	1.01	13.11	1.52	14.21	2.62
4-Br		11.60	12.63	1.03	13.12	1.52	14.29	2.69
4-F	7.76	11.62	12.57	0.95			14.11	2.49
H	7.78	11.64	12.54	0.90	13.04	1.40	14.14	2.50
4-Me	7.95	11.62	12.43	0.81	12.92	1.30	14.04 ^{d}	2.42 ^{d}
4-Buᵗ		11.68	12.44	0.76	12.92	1.14	14.00 ^{d}	2.32 ^{d}
4-MeO	8.07	11.62	12.33	0.71			13.89	2.27

^{a} From ref. 41a. ^{b} ±0.02 p.p.m. ^{c} ±0.03 p.p.m. ^{d} ±0.04 p.p.m. Peroxyformic acid, pK 7.1 (H₂O, 19.5 °C), from ref. 41b.
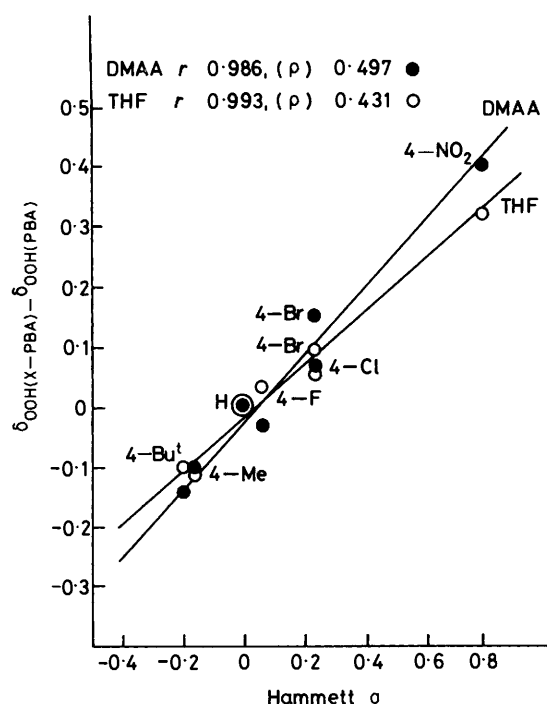

Figure 1. The difference in ¹H n.m.r. δOOH chemical shifts between para-substituted peroxybenzoic acid and peroxybenzoic acid in NN-dimethylacetamide (DMAA) and tetrahydrofuran (THF), respectively, as a function of Hammett σ constants. The ρ value is the slope of the correlation line (p.p.m./σ)

EX is the exchange repulsion interaction caused by exchange of electrons between A and B, PL is the polarization interchange, i.e. the effect of distortion of the electron distribution of A and B, and vice versa, CT is the charge transfer of electron delocalization interaction caused by the transfer of charge from occupied MOs of A to vacant MOs of B, and vice versa, and MIX is the coupling interaction, which is calculated as the difference between the total SCF interaction energy ΔE, and the sum of the above four components.[39] Mulliken populations were calculated by using all three basis sets.

Results and Discussion

¹H N.m.r.—N.m.r. has been widely used as a sensitive method for detecting and measuring hydrogen bonding.[40] The main experimental parameter which is of use in studying intermolecular hydrogen-bonded systems is the chemical shift.
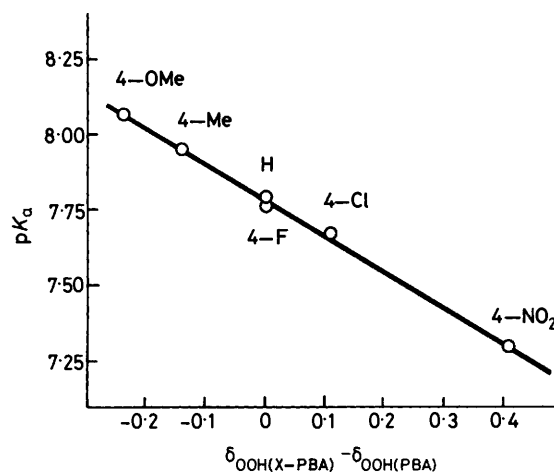

Figure 2. Plot of the pK_a values of peroxybenzoic acids versus the difference in δOOH chemical shifts between para-substituted peroxybenzoic acid and peroxybenzoic acid

It was thus of interest to investigate the change in the OOH proton chemical shift as a function of the acidity of peroxybenzoic acids, and of the donor strength of various oxygen bases.

In general, the observed chemical shift, δ_{obs}, corresponds to the population weighted average for the two states as indicated in equation (8), where α is the fraction of hydrogen-bonding acid

$$\delta_{obs} = \alpha\delta_{A-H} + (1 - \alpha)\delta_{A-H\cdots B} \qquad (8)$$

present in the monomeric state, and δ_{A-H} and $\delta_{A-H\cdots B}$ are the chemical shifts of non-complexed and the complexed acid, respectively. Under conditions of complete complexation of the acid, δ_{obs} equals $\delta_{A-H\cdots B}$. The quantity $\Delta_{A-H\cdots B}$ is then defined as the chemical shift of the hydrogen-bonded complex relative to the free acid ('hydrogen-bond shift') [equation (9)], and is

$$\Delta_{A-H\cdots B} = \delta_{A-H\cdots B} - \delta_{A-H} \qquad (9)$$

determined primarily by contributions from the complexation effect and the donor–anisotropy effect. The complexation effect always gives a downfield shift while the donor–anisotropy effect can lead to upfield or downfield shift. Thus, a shift to lower magnetic field is observed for all hydrogen-bonded systems involving electron donors in which magnetic anisotropic effects are small or absent.

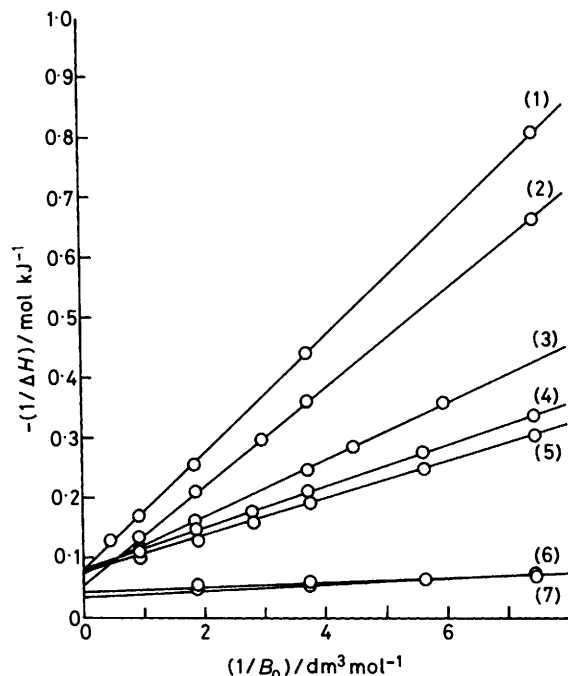An increased acidity of the acid component and an increased

Figure 3. Inverse plot of the enthalpy of complex formation, ΔH, of 4-chloroperoxybenzoic acid with various oxygen bases in carbon tetrachloride at 25 °C: (1) ethyl acetate (EA); (2) di-n-butyl ether (DBE); (3) dioxane (D); (4) tetrahydropyran (THP); (5) tetrahydrofuran (THF); (6) NN-diethylacetamide (DEAA); (7) tributyl phosphate (TBP). Three experimental points for (6) and (7) (at $1/B_0$ higher than 8) are not shown in the Figure. In all cases, correlation coefficients were better than 0.997

Table 2. The enthalpies, $\Delta H°$, and equilibrium constants, K, of hydrogen-bonded complexes between 4-chloroperoxybenzoic acid and various oxygen bases in carbon tetrachloride at 25 °C

Oxygen base	$-\Delta H°/\text{kJ mol}^{-1}$	$K/\text{l mol}^{-1}$	$\Delta\delta_{\text{OOH}}{}^a$
Ethyl acetate	12.3 ± 0.5	0.8 ± 0.2	0.63
Di-n-butyl ether	16.7 ± 0.9	0.7 ± 0.2	0.47
Dioxane	13.6 ± 0.5	1.5 ± 0.3	0.62
Tetrahydropyran	12.0 ± 0.5	2.4 ± 0.3	0.84
Tetrahydrofuran	12.9 ± 0.5^b	2.5 ± 0.5^b	1.09
Tributyl phosphate	22.9 ± 0.8	12.2 ± 1.0	1.57
NN-Dimethylformamide	25.0 ± 0.5	6.0 ± 0.5	2.42
NN-Dimethylacetamide	27.6 ± 0.5	8.5 ± 0.5	2.63
$3\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$	29.7 ± 0.5^c	9.9 ± 0.5^c	2.86
$4\text{-Bu}^t\text{C}_6\text{H}_4\text{CO}_3\text{H}$	26.3 ± 0.5^c	4.0 ± 0.5^c	2.32
NN-Diethylacetamide	25.9 ± 0.5	8.1 ± 0.5	2.53

^{a} Errors in $\Delta\delta_{\text{OOH}}$ are ±0.02 p.p.m. ^{b} Values reported here are somewhat lower compared with those in ref. 28 due to the presence of traces of an olefinic component in the tetrahydrofuran used at that time. ^{c} From ref. 28.
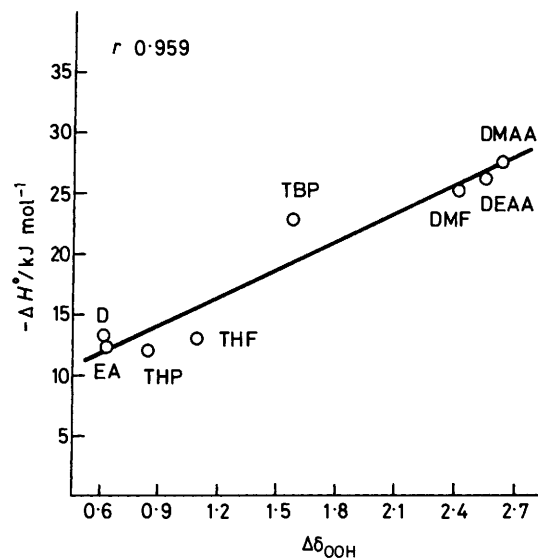
electron-donor strength of the base are expected to give larger complexation effect. The results of n.m.r. measurements for peroxy acid–oxygen base systems, although not corrected for carbonyl donor molecule anisotropy contributions to the 'hydrogen-bond shift' ($\Delta\delta_{\text{OOH}}$), confirm these predictions (Table 1).

The OOH absorptions of peroxybenzoic acids in inert solvents (CCl_4, CH_2Cl_2) are located as medium broad singlets at δ ca. 11.6 downfield from Me_4Si. These absorptions were completely concentration independent and were thus, in accord with previous observations,[7] assigned to the intramolecularly hydrogen-bonded form of the peroxy acid. The OOH proton chemical shift shows little sensitivity to the substituent, most probably due to the compensating effect; namely, with increasing electronegativity of the substituent there is both an increase in the acid strength and a decrease in electron density on the carbonyl oxygen atom.

On the other hand, the OOH proton was extremely sensitive to hydrogen bonding when organic oxygen bases were used as solvents. A downfield shift of this absorption indicated the formation of intermolecularly hydrogen-bonded complex. The sensitivity of the OOH chemical shift to substituent effects increased with increasing base strength. Excellent linear correlation were obtained by plotting OOH chemical shifts, i.e. $\delta\text{OOH(X-PBA)} - \delta\text{OOH(PBA)}$, of para-substituted peroxybenzoic acids in various organic oxygen bases, against the corresponding Hammett δ constants (Figure 1).

The substituent effect appears to be due mainly to the σ-bond induction and/or by through-space π-cloud anisotropy effects. In addition, OOH chemical shifts of substituted peroxybenzoic acids in NN-dimethylacetamide parallel peroxy acid strength $(\text{p}K)^{41}$ very well (Figure 2).

Figure 4. $-\Delta H°$ as a function of the hydrogen-bond shift, i.e. $\Delta\delta_{\text{OOH}}$, for complexes between 4-chloroperoxybenzoic acid and various oxygen bases

Calorimetry.—The equilibrium constants, K, and the enthalpies of complex formation, $\Delta H°$, obtained from inverse plots of $1/\Delta H$ versus $1/B_0$ (Figure 3) by linear regression, for 4-chloroperoxybenzoic acid with oxygen bases are collected in Table 2. Figure 4 shows that there is a good linear relation between $\Delta H°$ and $\Delta\delta\text{OOH}$ for 4-chloroperoxybenzoic acid–oxygen base adducts, at least within the range of values studied, i.e. from ca. 10 to 30 kJ mol^{-1}. The correlation is expressed by the least-square equation (10), and the correlation coefficient is

$$-\Delta H°/\text{kJ mol}^{-1} = (7.59 \pm 0.92)\Delta\delta\text{OOH} +$$
$$(7.35 \pm 1.61) \quad (10)$$

0.959. However, it should be pointed out that chemical shifts, uncorrected for anisotropy contributions for complexes of carbonyl bases, are plotted against $\Delta H°$, and that even small changes in the chemical shifts of the complexes at the end of the line (DMF, DMAA, DEAA) would change the slope and the intercept significantly. It should also be noted that the experimentally obtained value $\Delta H°$ is the sum of two

Table 3. Calculated structures

Parameter	STO-4G	4-31G*	4-31G**	STO-4G		STO-4G	4-31G*	4-31G**
r(C–H) (Å)	1.0900	1.0848	1.0866	1.0910		1.0898[a]	1.0900[a]	1.0900[a]
r(C=O) (Å)	1.2250	1.1707	1.1707	1.2361				
r(C–O) (Å)	1.4035	1.3320	1.3321	1.3278		1.4387	1.3962	1.3970[a]
r(O–O) (Å)	1.4036	1.3953	1.3943	1.4724				
r(O–H) (Å)	0.9992	0.9510	0.9461					
∠(H–C=O) (°)	127.21	126.01	126.04	119.39				
∠(O=C–O) (°)	122.71	127.14	127.06	129.93	∠(COC)	110.72	115.49	115.54
∠(C–O–O) (°)	106.90	110.89	110.90	115.21				
∠(O–O–H) (°)	98.71	99.61	99.86					
E_T, hartrees	−261.875 39	−263.258 03	−263.266 53	−261.109 73		−153.212 90	−153.911 78	−153.922 47

[a] The staggered conformation (∠2-1-3-6 180°, ∠3-1-2-9 0°) has been found to possess the lowest energy. The tetrahedral angle in the methyl group was not optimized (109.47°).
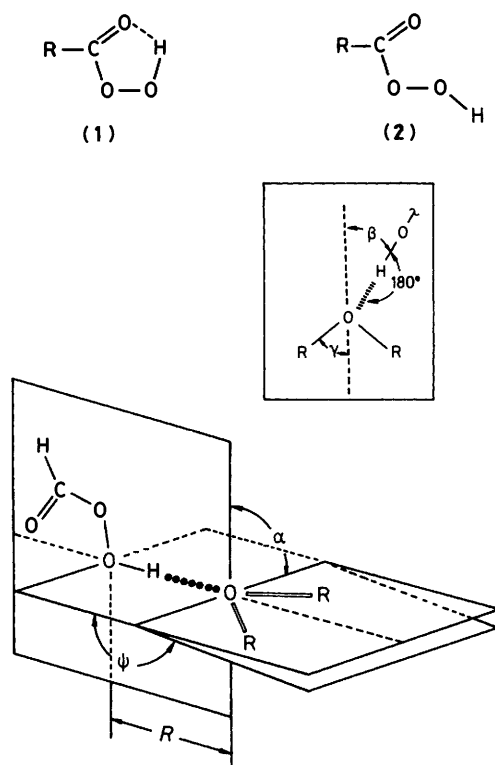

Figure 5. Geometrical variables with respect to which the geometry of the complex peroxyformic acid–dimethyl ether was optimized

contributions, i.e. a presumably endothermic opening of the chelate ring in the intramolecularly hydrogen-bonded form of the peroxy acid (1), to form the conformer (2) (see discussion below), and an exothermic contribution due to the formation of the intermolecularly hydrogen-bonded complex.

Molecular Orbital Studies.—The geometries of various conformers of peroxyformic acid were calculated previously by using *ab initio* methods of different degrees of sophistication.[8–18]

The planar *syn* conformer (1), with the intramolecular hydrogen bonding, has been found to possess the lowest energy by using extended basis sets.[18] Since the chelate ring opens after complexation with the oxygen base, we searched for the most stable opened form of peroxyformic acid. We found that in the

framework of the STO-4G calculations, the planar *anti* form (2), obtained from the chelated one by 180° rotation about the O–O bond, has the lowest energy. We have optimized the geometry of (2) with the 4-31G* and 4-31G** basis sets. It is interesting to mention that this conformer has even been suggested to be the most stable conformation of peroxyformic acid (PCILO,[15] 4-31G,[12] 5-31G[17,42]). However, recent microwave[18] and *ab initio* studies showed that the most stable conformation is characterized by an intramolecular hydrogen bond (1). Namely, conformer (1) has been found to be more stable than conformer (2) by 6.3 kJ mol⁻¹(4-31G)[14,16] and 17.5 kJ mol⁻¹(4-21G*),[18] respectively. Although the O–O rotational barriers in peroxy acids are not known for certain at present, there is some indication from *ab initio* MO studies that they are in the range 4—9 kJ mol⁻¹ in peroxyformic acid[16,17] and 12—17 kJ mol⁻¹ in peroxyacetic acid.[10,11]

We have also optimized the geometry of dimethyl ether. The geometrical parameters of all these species are, together with those of peroxyformate ion, collected in Table 3.

Except for the C–O–C angle in dimethyl ether, which was optimized in the complex only at STO-4G level of calculations, all other geometrical parameters in the monomers were held rigid for all other calculations. The hydrogen bond was assumed to be linear (O–H ··· O = 180°) since, except in very strained systems, the optimum hydrogen-bond angle, calculated for 1:1 complexes, has always been very nearly linear.[43,44]

The procedure was to minimize all geometrical variables, shown in Figure 5 as a function of distance R. Since 4-31G* optimization of α and β in the complex is not practical, we have used the predicted STO-4G values for these parameters.

The equilibrium geometries and energies of the complex are, together with results of the energy decomposition analysis, collected in Table 4.

The calculated intermolecular distance R is in excellent agreement with the value 2.609 Å found in p-nitroperoxybenzoic acid–triphenylphosphine oxide complex as determined by X-ray crystallography.[20]

It appears that there is some 'directional influence' of the lone pairs on the sp^3-hybridized oxygen atom of dimethyl ether.* Although the optimum value of β and ψ could depend on the basis set, it is interesting to mention that similar observations

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* One would expect ψ ≈ 125° if hydrogen bonding is assumed to take place in the direction of the sp^3-hybridized lone pair of the oxygen atom. It is interesting to mention that ψ = 129.3° in the peroxyformic acid–water complex (STO-4G) [α 90°; β 0°; γ 49.9°; r(O–H) 0.987 Å; R 2.601 Å; ΔE −36.03 kJ mol⁻¹].

Table 4. Equilibrium geometries, energies, and interaction energies of the peroxyformic acid–dimethyl ether complex

Parameter	STO-4G	4-31G*
α (°)	90	90
β (°)	0	0
γ (°)	56.0	57.7
R/Å	2.593	2.796
ψ (°)	146.1	147.1
E_T/hartree	−415.101 96	−417.183 49
ΔE/hartree	−0.013 67	−0.013 68
ΔE/kJ mol⁻¹	−35.90	−35.90
ΔE(energy components)/kJ mol⁻¹	ES, −53.51; EX, 87.28 PL, −2.13; CT, −60.25 MIX, −7.28	

Table 5. The net atomic charges (e, × 10³)[a]

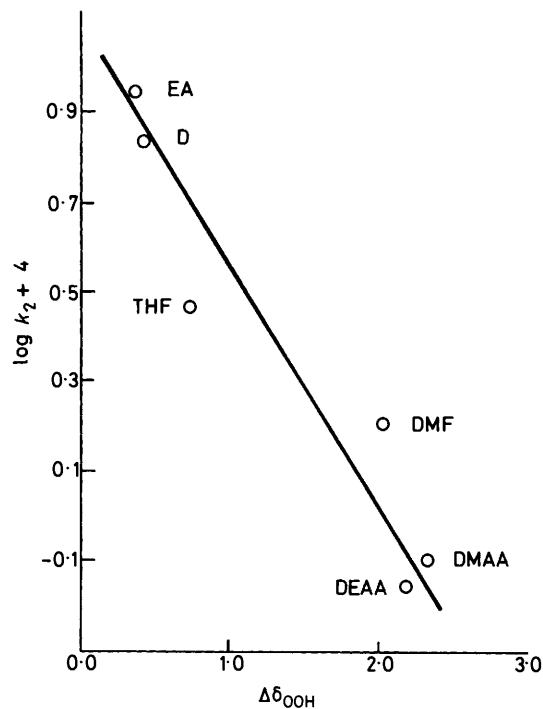| Atom	STO-4G	4-31G*	4-31G**	STO-4G	STO-4G	4-31G*
H(1)	88	191	143	−33	75	180
C(2)	254	581	646	211	249	582
O(3)	−224	−487	−498	−393	−239	−496
O(4)	−163	−366	−375	−321	−182	−375
O(5)	−171	−389	−282	−463	−234	−448
H(6)	216	470	366		258	519
O(1)	−247	−617	−640		−256	−639
C(2)	−78	−147	14		−73	−145
C(3)	−73	−144	17		−69	−141

[a] The term net atomic charge is defined as $Z - n$ (STO-4G, 4-31G*, or 4-31G**), where Z is the atomic number and n is the net electronic density of an atom.

Figure 6. Plot of log k_2 for the epoxidation of cyclohexene with 4-t-butylperoxybenzoic acid in various oxygen bases as solvents at 20 °C versus the hydrogen-bond shifts, $\Delta\delta_{OOH}$, for this peroxy acid in the corresponding oxygen bases

were made in other MO studies of hydrogen-bonded complexes by using extended basis sets,[45] as well as in X-ray crystallographic studies.[46]

Qualitatively, the complex is predominantly ES-CT in nature. The interaction energy, ΔE, consists of 43% ES, 49% CT, 2% PL, and 6% MIX. While electrostatic component of the interaction energy is regarded rather well represented with the STO-4G (4-31C and 6-31G exaggerate it), the polarization component might be somewhat underrepresented. The STO-4G gives, however, a rather substantial overestimate of CT as compared with the extended basis sets.[30]

Net atomic charges (Mulliken populations) due to the hydrogen-bond formation have also been calculated and are, together with net atomic charges of free molecules, collected in Table 5. A net charge transfer of 0.072 e (STO-4G) and 0.038 e (4-31G*), respectively from dimethyl ether to peroxyformic acid was found. Hydroxylic oxygen [O(5)] of peroxy acid and ether oxygen gain charge, while hydroxylic hydrogen and ether carbons lose it. These observations are in accordance with the findings in other intermolecularly hydrogen-bonded 1:1 complexes with hydrogen bonds of similar strengths.

The hydrogen atom involved in the hydrogen bonding is believed to be significantly more strongly bound to the peroxy

acid part of the complex. The formation of the complex forces a moderately large negative charge on the peroxycarboxy fragment, largely on the oxygen atom of the OH group [O(5)]. To compare the extent of this charge shift, we have also investigated peroxyformate ion. It is evident from Table 5 that a fully developed anionic centre on the O(5) atom of the peroxycarboxylate ion bears, at least at the STO-4G level of calculations, larger negative charge compared with the one on the same oxygen atom in the complex.

Kinetic Studies.—Kinetic and activation parameters for the oxidation of cyclohexene by t-butylperoxybenzoic acid in organic oxygen bases as solvents are collected in Table 6.

It is clearly evident from Figure 6 that the strength of the intermolecular association between the peroxy acid and base plays a predominant role in these reactions.

The peroxy acid isotope effect for epoxidation of this olefin, with 4-Bu^tC₆H₄COOOH(D) in NN-dimethylacetamide at 20 °C, of k_H/k_D 1.09 (OH/OD) seems to indicate that hydrogen transfer is not occuring in the rate-determining step of the epoxidation mechanism.[47] † A small primary peroxy acid isotope effect of 1.17 has already been reported for the epoxidation of p-phenylstyrene with 3-chloroperoxybenzoic

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† Two possible opposing effects upon $(k_H/k_D)_{obs}$ are operating if one assumes that intramolecularly hydrogen-bonded form of peroxy acid is the reactive species, i.e. in the peroxy acid–base equilibrium [equation (1)], K_H/K_D is expected to be less than one, while $k_H/k_D > 1$ if proton transfer occurs in the transition state for epoxidation. Since $(k_H/k_D)_{obs} = (k_H/k_D) \times (K_H/K_D)$, the latter two terms tend to cancel each other and would thus make the interpretation of a small $(k_H/k_D)_{obs}$ value difficult. Since our kinetic experiments were done under conditions of complete complexation of the peroxy acid, and by assuming that the complex is the reacting species, the danger of the misinterpretation of a small isotope effect appears to be remote.

Table 6. Rate constants and activation parameters for the oxidation of cyclohexene with 4-t-butylperoxybenzoic acid in various oxygen bases as solvents; $\Delta\delta_{OOH}$ for 4-t-butylperoxybenzoic acid

Solvent	$10^4 k_2 (20\,°C)/l\ mol^{-1}\ s^{-1}$		$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$\Delta S^{\ddagger}/J\ mol^{-1}\ K^{-1}$	$\Delta\delta_{OOH}$
Carbon tetrachloride	37.5		43.5	−142.2	(11.68)
Ethyl acetate	8.85		55.6	−112.5	0.43
Dioxane	6.71		59.0	−103.3	0.44
Tetrahydrofuran	2.80		61.1	−103.8	0.74
NN-Dimethylformamide	1.61		64.8	−94.6	2.09
NN-Dimethylacetamide	0.80		68.6	−82.4	2.34
4-Bu^{t}C$_6$H$_4$CO$_3$D	0.73	k_H/k_D 1.09			
NN-Diethylacetamide	0.72		71.5	−78.7	2.19

[a] Errors (standard deviations) in k_2 are ±3%, those in $\Delta H^{\ddagger}$ are ±4 kJ mol⁻¹, those in $\Delta S^{\ddagger}$ are ±11 J mol⁻¹ K⁻¹, and those in $\Delta\delta_{OOH}$ are ±0.05. Concentration of reactants, 0.5—2.5 × 10⁻²M.
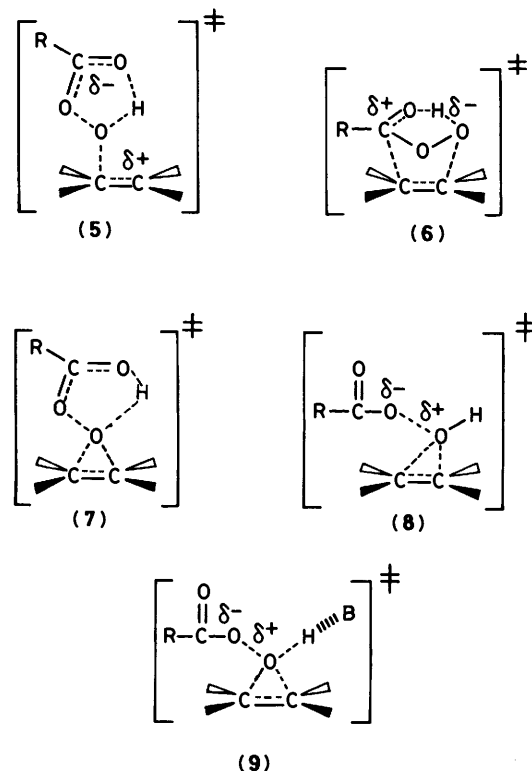

Scheme.
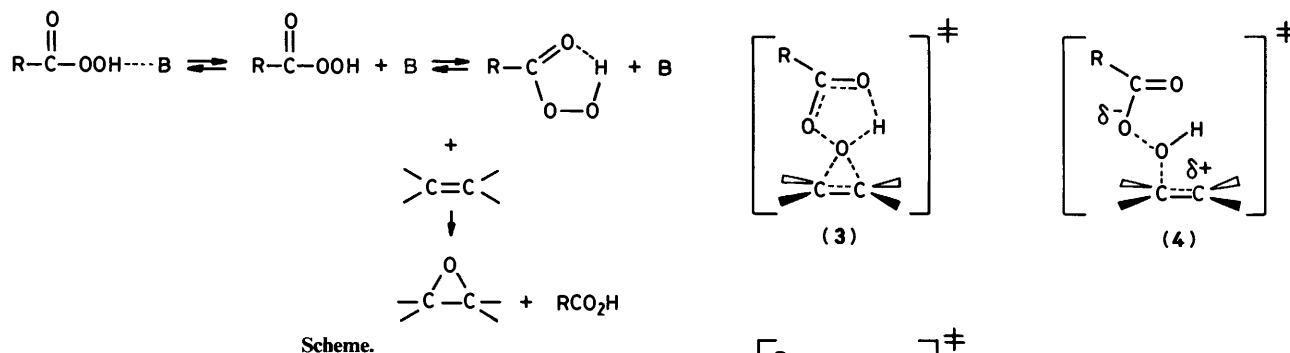
acid in an inert solvent (1,2-dichloroethane).[48] According to Westheimer's model of proton-transfer reactions, the k_H/k_D will approach the value of 1 for the reactant-like transition state and will increase to a maximum value of ca. 7 for a symmetrical transition state, and drop again to a value of ca. 1 for a product-like transition state.[47] Clearly, the first and the last possibility should be considered for epoxidation with peroxy acids both in 'inert' solvents as well as solvents capable of forming inter-molecularly hydrogen-bonded complexes with these reagents.

The nature of the reduced reactivity of peroxy acids after complexation with organic oxygen bases, already reported for various substrates,[21—24,27] has not yet been clarified unambiguously. It has been suggested that the complexation reduces the concentration of the 'effective' intramolecularly hydrogen-bonded form of peroxy acid, and that higher activation enthalpies observed in these reactions, compared with reactions run in 'inert' solvents, reflect desolvation processes on going from reactants to the transition state.[23,24] The corresponding 'dissociation mechanism' is shown in the Scheme. Intra-molecular proton transfer has been suggested as a mechanistic possibility at various times. Bartlett was the first to suggest a very delocalized and symmetrical transition state (3).[49] On the basis of kinetic isotope effect studies, Hanzlik and Schearer concluded that the transition state for epoxidation is unsymmetrical and involves little movement of the peroxy-carboxylic hydrogen atom (4).[48] Ab initio calculations of the interaction between peroxyformic acid and ethylene indicated an 'early'-type transition state with little reorganization in both participating molecules (5).[13,50] Involvement of a more or less developed proton transfer prior to the transition state for the rate-determining step of epoxidation mechanism, with the formation of a more or less developed hydroxycarbonyl oxide, was first suggested by Kwart et al.[51] A 1,3-dipolar addition-type transition state is represented as (6). A symmetrical or unsymmetrical transition state (7) with nearly complete proton transfer and involving an 'electrophilic' rather than 'nucleophilic' oxygen atom would also be in accord with the observed peroxy

acid isotope effect. Mimoun has recently proposed dioxiranes derived from hydroxycarbonyl oxides, as the reacting species in oxidations with peroxy acids.[20]

Waters was the first to suggest that the attack of the substrate on peroxy acid need not necessarily involve the chelated form of the reagent, and also suggesting an opened transition state (8).[52] It appears that, in view of the relatively low O–O rotational barrier in peroxy acids, such a presumption is quite reasonable. Indeed, recent reports by Bruice et al. indicate that intra-

molecular proton transfer does not provide a driving force for mono-oxygen transfer from peroxy acids to alkyl sulphides, tertiary amines, or iodide ion.[53]

Although intramolecular proton transfer prior to the transition state of the rate-determining step for epoxidation is at least theoretically feasible in the gas phase or in 'inert' solvents, and that even some pre-equilibrium formation of a low concentration of the monomeric form of peroxy acid from the complex cannot be completely ruled out, it seems nevertheless more plausible that, at least under conditions of complete complexation, the adduct rather than monomeric form of peroxy acid is the reacting species. A charge-transfer-type 'early' transition state (9) of a 'direct attack mechanism', already proposed previously,[26] would seem to be in accord with all the available experimental and theoretical evidence available on epoxidation with peroxy acids in organic oxygen bases as solvents.

Conclusions.—Although detailed mechanistic features of epoxidation with peroxy acids remain elusive, there seems to be a consensus of the opinion that these reagents are capable of delivering an 'electrophilic' oxygen to the substrate. The results of the present calorimetric and ^{1}H n.m.r. studies clearly showed that peroxy acids form relatively strong intermolecularly hydrogen bonded complexes with organic oxygen bases, and that the strength of these associations is sensitive on the acidity of the peroxy acid and the basicity of the oxygen base. A small peroxy acid isotope effect in the epoxidation of cyclohexene with 4-Bu^{t}C$_6$H$_4$CO$_3$H(D) (k_H/k_D 1.09) in NN-dimethylacetamide, together with other evidence from kinetic and *ab initio* molecular orbital studies on peroxyformic acid–dimethyl ether complex, seem to indicate that oxygen base is most probably a part of an 'early' charge-transfer-type transition state for epoxidation in these bases as solvents, and that the reduced reactivity of peroxy acids in these systems most probably reflects the forcing of the enlarged negative charge on the O–H oxygen atom, thus lowering the 'electrophilicity' of the reacting centre in peroxy acid. Increasing entropies of activation for epoxidation of cyclohexene, when going from less to more basic solvents, if real, would seem to suggest that the more strongly hydrogen-bonded complexes form transition states that are looser with respect to the reacting components than do the less strongly hydrogen-bonded adducts. Whether these interactions actually involved charge-transfer or π-complexes in these reactions remains to be elucidated.

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