tra of benzophenone and benzhydrol showed that the aromatic protons of the former absorb further downfield than those of the latter, so that the presence of a small amount of benzophenone in the sample would not interfere with the deuterium analysis.

Carbonation of the Remaining Grignard Reagent.—The carbonation was begun 20 min after the reaction of the Grignard reagent with 0.5 equiv of benzophenone. Crushed Dry Ice contained in a 250-ml erlenmeyer flask was slowly added through Gooch tubing to the unconsumed Grignard reagent contained in a round-bottomed flask equipped with condenser and mechanical stirrer. Once all the Dry Ice had been added, the reaction mixture was allowed to attain room temperature overnight.

The mixture was then treated with 6 *N* hydrochloric acid until two clear layers separated. The aqueous layer was extracted several times with ether, and the extracts were combined with the organic layer. The yield of norbornyl acid was 62% of the theoretical amount as determined by titration of an aliquot of the ethereal solution in 65% methanol with standard sodium hydroxide solution to a phenolphthalein end point. The solution of norbornyl acid was then extracted with three 50-ml portions of 2 *N* sodium hydroxide solution and one 50-ml portion of water. The combined base extracts were held for the methylation step.

Reaction of Norbornyl Acid with Diazomethane.—Diazomethane was prepared from Diazald (21.5 g, 0.1 mol).[19]

Just prior to the reaction with diazomethane, the norbornyl acid was liberated from the sodium salt by acidification and extraction with ether. Esterification was accomplished by the dropwise addition of the dried norbornyl acid solution to diazomethane at 0°. The mixture was allowed to stand until nitrogen was no longer evolved and was then treated with 3 *M* sulfuric acid until the disappearance of the yellow color. The two layers were separated, and the aqueous layer was extracted several times with ether. The extracts were combined with the organic layer, washed with two 50-ml portions of 0.05 *M* sodium carbonate solution, and then dried ($MgSO_4$). The ethereal solution was then filtered, combined with an ether wash of the magnesium sulfate, and concentrated by distillation at atmospheric pressure. Analysis of the residual oil by glpc gave one peak, with a retention time of 9.5 min. Glpc analysis was carried out using a 6 ft × 0.25 in., 15% Apiezon L on Chromosorb W-HP, 80–100 mesh column coupled to a 6 ft × 0.25 in., 20% Carbowax 20M on Chromosorb W-HP, 80–100 mesh column, 210°, 120 ml/min He flow rate. An authentic sample of the methyl ester of *endo*-norbornane-2-carboxylic acid gave one peak with the same retention time, whereas a mixture of the endo and exo isomers gave a second peak at 12.0 min. Analysis of the oil was repeated using a 10 ft × 0.25 in. column of 25% castorwax on 60–80 Chromosorb P at 120° and 60 ml/min. One peak was observed at 73 min, the retention time of the endo isomer under these conditions.

Dehydrohalogenation of Monodeuterated *exo*-2-Chloronorbornane.—Potassium (3 g, 0.075 mol) was slowly introduced under nitrogen into a dry flask containing 3-methyl-3-pentanol (51 g, 0.5 mol) and equipped with condenser and magnetic stirrer. As the concentration of potassium alkoxide increased, the solution acquired a reddish-brown hue, and the reaction became less vigorous. Completion of reaction was effected by heating.

Monodeuterated *exo*-2-chloronorbornane (6.6 g, 0.05 mol) was added all at once to the solution of potassium alkoxide, and the mixture was refluxed under nitrogen for 1 hr. Refluxing was then continued for a total of 17 hr while sweeping continuously with nitrogen. The norbornene (0.6 g) which formed was scraped from the inner surface of the condenser and from the tube leading into a trap cooled with a Dry Ice–isopropyl alcohol mixture.

Glpc analysis of an ether solution of the collected norbornene indicated the presence of less than 1% 3-methyl-3-pentanol. The sample was analyzed for deuterium content by low voltage mass spectroscopy, 0.46 deuterium atoms per molecule.

Registry No.—**2a,** 33495-71-5; **2b,** 33495-72-6; *exo*-**4a,** 33495-73-7; *endo*-**4a,** 33495-74-8; *exo*-**4b,** 33495-75-9; *endo*-**4b,** 33495-76-0; benzophenone, 119-61-9.

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The Nucleophilic Reactivity of Peroxy Anions[1]

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We report rate data on the reactivity of several peroxy anions with the anions of bromoacetic acid, α-bromo-*p*-toluic acid, *p*-cyanobenzoic acid, *p*-nitrophenylsulfuric acid, and with *p*-nitrophenylacetate and 2,4-dinitrochlorobenzene. The magnitude of the α effect, as measured by the ratio log (k_{HOO^-}/k_{HO^-}), appears to be linearly correlated with the magnitude of the product $|\alpha\beta|$ of the coefficients of the Edwards equation (the oxibase scale): $\log k/k_0 = \alpha E_n + \beta H$.

Edwards and Pearson[3] recognized a class of nucleophiles which showed exceptionally high reactivity toward a variety of substrates relative to their basicity toward hydrogen. This class is structurally characterized by an unshared pair of electrons on the atom adjacent or α to the nucleophilic atom. This rate enhancement is known as the α effect. Both uncharged nucleophiles such as hydrazine and hydroxylamine as well as anionic nucleophiles such as the peroxy anions exhibit this effect but to varying degrees toward various substrates. There have been a number of recent discussions of the α effect.[4] In this study, we have examined the reactivity of the anions of hydrogen peroxide, methyl hydroperoxide, *tert*-butyl hydroperoxide, and several peroxycarboxylic acids toward several substrates with a view toward defining more precisely the factors influencing the magnitude of the α effect.

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Table I

Reactions of Nucleophiles with α-Bromo-*p*-toluic Acid at 25°[a]

Nucleophile	pK_a'	pH range	Nucleophile concn, *M*	Substrate concn, *M*	k_2, M^{-1} min^{-1}
p-Methoxyperoxybenzoic acid	7.8	9.04–9.36[b]	$3.5\text{–}6.5 \times 10^{-3}$	4.9×10^{-4}	3.8 ± 0.1
m-Chloroperoxybenzoic acid	7.4	9.04–9.36[b]	$3.05\text{–}6.05 \times 10^{-3}$	4.9×10^{-4}	4.0 ± 0.3
p-Nitroperoxybenzoic acid	7.1	9.04–9.36[b]	$2.47\text{–}4.26 \times 10^{-3}$	4.9×10^{-4}	4.0 ± 0.3
Peroxyacetic acid	8.2	9.95[b]	$5.6\text{–}11.4 \times 10^{-3}$	5×10^{-4}	1.5 ± 0.1
HOO^-	11.37	10.98–11.42[c]	$3.13\text{–}6.05 \times 10^{-2}$	$9.4\text{–}10.7 \times 10^{-4}$	2.1 ± 0.2[d]
$MeOO^-$	11.08	11.07–11.36[c]	$4.7\text{–}6.7 \times 10^{-2}$	$9.6\text{–}9.9 \times 10^{-4}$	1.8 ± 0.1
tert-$BuOO^-$	12.46	11.78–12.14[c]	$8.85\text{–}9.17 \times 10^{-2}$	1.02×10^{-3}	1.5 ± 0.2
HO^-	15.74	12.66–13.43[c]		1.1×10^{-3}	0.16 ± 0.01[e]
H_2O	−1.74		55.5	1.1×10^{-3}	4.3×10^{-6}

[a] EDTA (2×10^{-4} *M*) was present in all runs. The ionic strength was made up to 1.0 with KCl or $NaClO_4$. [b] Carbonate buffer. The blank correction, due largely to the buffer, was in the range 25–30%. [c] pH adjusted with NaOH. [d] Activation parameters for the temperature range 10–30°: $\Delta H^{\ddagger} = 15$ kcal mol^{-1}; $\Delta S^{\ddagger} = -15$ cal mol^{-1} deg^{-1}. [e] Activation parameters for the temperature range 15–40°: $\Delta H^{\ddagger} = 18$ kcal mol^{-1}; $\Delta S^{\ddagger} = -9$ cal mol^{-1} deg^{-1}.

Table II

The Reaction of Nucleophiles with Bromoacetic Acid at 40°[a]

Nucleophile	pK_a'	pH range	Nucleophile range, *M*	10^2k_2, M^{-1} min^{-1}
HO^-	15.27		0.1–0.3	2.2 ± 0.05
HOO^-	11.18	12.5–12.6[b]	$1\text{–}4 \times 10^{-2}$	28 ± 0.3
tert-$BuOO^-$	12.22	12.6[b]	$5\text{–}20 \times 10^{-3}$	10 ± 0.2
m-Chloroperoxybenzoic acid	7.6	10.3–10.5[c]	$1.5\text{–}4 \times 10^{-2}$	6.7 ± 0.05
$CH_3CO_3^-$	8.2	10.5[c]	$2\text{–}3.2 \times 10^{-2}$	9.1 ± 0.1

[a] EDTA (2×10^{-4} *M*) was present in all runs. The ionic strength was made up to 0.55 with KNO_3. Substrate was 5×10^{-4} *M*. [b] pH adjusted with NaOH. [c] Carbonate buffer. The blank correction was in the range of 1%.

Results and Discussion

Saturated Carbon.—Our results for displacement at tetrahedral carbon are given in Tables I and II. We have used two substrates, α-bromo-*p*-toluic acid and bromoacetic acid, and find for both that the ratio k_{HOO^-}/k_{HO^-} in water is about 13. This ratio is to be compared with the value of 35 for the reaction with benzyl bromide in 50% acetone–water as solvent.[5] Tables I and II show that the relative rate with which the aromatic and aliphatic peroxycarboxylic acid anions attack the substrate is dependent upon the substrate; the anion of peroxyacetic acid is more reactive than the anion of *m*-chloroperoxybenzoic acid when the substrate is bromoacetic acid, whereas this relative rate is reversed for the aromatic substrate, α-bromo-*p*-toluic acid. We attribute this phenomenon to an interaction of the aromatic rings (ref 4h, p 415). The order of reactivity for bromoacetic acid follows the basicity order with the exception of *tert*-butyl hydroperoxide. *tert*-Butyl hydroperoxide is generally less reactive than expected for its basicity and this can be reasonably attributed to steric factors. A significant exception in the literature is in the reaction with tetranitromethane, but in this case Sager and Hoffsommer[6] have demonstrated that the attack is at the outer oxygen atom where steric effects are minimized. The Brønsted slope for a reaction of this type is small.[4e] In fact, the rate constants for the three substituted peroxybenzoic acids with α-bromo-*p*-toluic acid are essentially identical although their acidities vary by about a factor of five.

Carbonyl Carbon.—Table III gives our results for the reaction with *p*-nitrophenylacetate. This substrate was chosen for a comparative study of the reaction of peroxyanions with carbonyl carbon because of the extensive previous work on this compound.[7] Our data coincide reasonably well with the literature data when allowance is made for the differences in the pK_a values used.

Tetrahedral Sulfur.—Table IV presents our data for *p*-nitrophenyl sulfate. Benkovic and Benkovic[8] find $k_{HO^-} = 3 \times 10^{-6}$ and $k_{H_2O} = 2.7 \times 10^{-9}$ M^{-1} min^{-1} at 35°. The very large value for k_{HOO^-}/k_{HO^-} compared with k_{MeOO^-}/k_{HO^-} is notable in view of the relatively small value of the Brønsted slope (0.2).[8] We feel that this is attributable either to a relatively large contribution to stabilization of the transition state by hydrogen bonding in the case of the anion of hydrogen peroxide, or, as has been argued for attack at tetrahedral phosphorus,[9] due to an increased dependence on steric factors relative to carbonyl carbon.

Nitrile Carbon.—We have reported recently[10] a study of the kinetics of the reaction of hydrogen peroxide with the nitrile, *p*-cyanobenzoic acid, together with labeling experiments using $H^{18}O^{18}OH$. We report here values for k_{HOO^-}/k_{HO^-} of 900–1200 depending on temperature (Table V). Wiberg's value[11] for this ratio varies from about 20,000 to 66,000, depending on the nitrile used. The value of 66,000 has been widely quoted as an extreme example of the α effect. We can compare our data for *p*-cyanobenzoic acid in water with Wiberg's data for benzonitrile in 50% aqueous acetone, since the σ constant for *p*-COO^-

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TABLE III

REACTIONS OF NUCLEOPHILES WITH *p*-NITROPHENYLACETATE[a]

Nucleophile	Temp, °C	$10^{-3}k_2$, M^{-1} min^{-1}
HOO^-[b]	25	68 ± 3[c]
HOO^-	30	75 ± 3
HOO^-	35	93.5 ± 3
HOO^-	40	107.5 ± 5
HOO^-	45	115 ± 2
CH_3OO^-[d]	25	19 ± 0.6[e]
CH_3OO^-	44.5	50 ± 4
$(CH_3)_3COO^-$[f]	25	4.6 ± 0.2[g]
$(CH_3)_3COO^-$	35	6.8 ± 0.5
$(CH_3)_3COO^-$	45	8.9 ± 0.5
MCPB[h]	8	1.7 ± 0.05[i]
MCPB	15	2.6 ± 0.05
MCPB	20	3.5 ± 0.05
HO^-[j]	20	0.715 ± 0.02[k]
HO^-	25	0.88 ± 0.04
HO^-	32	1.26 ± 0.15
HO^-	40	1.79 ± 0.2

[a] EDTA (1×10^{-3} *M*) was present in all cases. The ionic strength was made up to 1.0 with KCl. Runs in the vicinity of pH 7 were conducted in phosphate buffer. We find k_2 for HPO_4^{2-} at 25° = 1×10^{-2} M^{-1} min^{-1}. Runs in the vicinity of pH 9.5 were conducted in carbonate buffer. See footnote *j*. [b] The nucleophile concentration range was 5×10^{-3} to 1.7×10^{-2} *M* (uncorrected for the fraction ionized). Substrate concentration was 1×10^{-3} *M*. The pH range was 6.7–7.0. [c] $\Delta H^{\ddagger}$ = 5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −28 cal mol^{-1} deg^{-1}. [d] The nucleophile concentration range was 1.6×10^{-2} to 7.0×10^{-2} *M* (uncorrected for the fraction ionized). Substrate concentration was 1×10^{-3} *M*. The pH range was 6.3–7.0. [e] $\Delta H^{\ddagger}$ = 8.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −20 cal mol^{-1} deg^{-1}. [f] The nucleophile concentration range was 1.5×10^{-2} to 7.0×10^{-2} *M* (uncorrected for the fraction ionized). Substrate concentration was 1×10^{-3} *M*. The pH range was 7.3–7.8. [g] $\Delta H^{\ddagger}$ = 6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −31 cal mol^{-1} deg^{-1}. [h] MCPB is *m*-chloroperoxybenzoic acid. The nucleophile concentration range was 8×10^{-5} to 1.6×10^{-4} *M*. Substrate concentration was 2 to 2.5×10^{-5} *M*. The pH range was 9.4–9.5. [i] $\Delta H^{\ddagger}$ = 9 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −17 cal mol^{-1} deg^{-1}. [j] Runs were made at constant pH values (9.4–9.7) for each temperature at five carbonate buffer concentrations (0.266, 0.20, 0.133, 0.067, and 0.033 *M*). Extrapolation to [B] = 0 gave k_{HO^-} for that temperature. $k_{CO_3^{2-}}$ values follow: 20°, 0.514; 25°, 0.81; 32°, 1.5; 40°, 2.75 (M^{-1} min^{-1}). Substrate concentration was 1×10^{-4} *M*. [k] $\Delta H^{\ddagger}$ = 8 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −26 cal mol^{-1} deg^{-1}. Tommila and Hinshelwood[7b] give $\Delta H^{\ddagger}$ = 10 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −19.5 cal mol^{-1} deg^{-1} for the reaction in 60% aqueous acetone.

TABLE IV

REACTIONS OF NUCLEOPHILES WITH *p*-NITROPHENYL SULFATE AT 50°[a]

Nucleophile	10^5k_2, M^{-1} min^{-1}
HOO^-[b]	200 ± 20
CH_3OO^-[c]	65 ± 5
$(CH_3)_3COO^-$[d]	52 ± 2
HO^-[e]	1.6 ± 0.2

[a] EDTA (1×10^{-3} *M*) was present in all runs. The ionic strength was made up to 1.0 with KCl. [b] Runs were made in 0.825 *M* NaOH containing 1×10^{-3} *M* substrate and from 6×10^{-2} to 1.2×10^{-1} *M* total hydrogen peroxide. [c] Runs were made in 0.838 *M* NaOH containing 8×10^{-4} to 3.2×10^{-3} *M* substrate and from 1.2×10^{-1} to 2.4×10^{-1} *M* methyl hydroperoxide. [d] Runs were made in 0.839 *M* NaOH containing 8×10^{-4} to 3.2×10^{-3} *M* substrate and 1.5×10^{-1} *M* *tert*-butylhydroperoxide. [e] NaOH concentration was varied from 0.25 to 1.04 *M*.

TABLE V

THE REACTION OF *p*-CYANOBENZOIC ACID WITH HOO^- AND HO^-

Nucleophile	Temp, °C	k_2, M^{-1} min^{-1}
HO^-	50	0.045[a]
HO^-	45	0.031
HO^-	35	0.013
HO^-	25	0.0055
HOO^-	60	75[b]
HOO^-	50	41
HOO^-	40	22.5
HOO^-	25	6.5

[a] Solutions were 6×10^{-5} *M* in nitrile and 0.01–1.0 *M* in NaOH. μ = 1.0. $\Delta H^{\ddagger}$ = 15 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −25 cal deg^{-1} mol^{-1}. [b] Runs with hydrogen peroxide were in phosphate buffer in the pH range 6.7–7.4, μ = 0.25. An increase in the ionic strength to 1.0 decreased the rate constant by about 10%. The runs at 25 and 40° were 5×10^{-3} *M* in H_2O_2, 5×10^{-2} *M* in nitrile, and 5×10^{-5} *M* in EDTA. The runs at 50 and 60° were 0.1 *M* in H_2O_2, 0.05 *M* in nitrile, and 1×10^{-3} *M* in EDTA. The error in the rate constants is of the order of 5%. We have reported[10] a rate constant of about 1 M^{-1} min^{-1} for the reaction at 25° at pH values of 10 and above. We think that under these conditions the second step in the process becomes rate limiting because of a reduction in the concentration of the un-ionized peroxycarboximidic acid. $\Delta H^{\ddagger}$ = 13 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −19 cal deg^{-1} mol^{-1}.

is close to zero.[12] The data of Table V show that the difference between Wiberg's ratio and ours at 50° arises approximately equally from differences in k_{HO^-} and in k_{HOO^-}. Our value for k_{HO^-} is larger than Wiberg's by a factor of 6.7, while our value for k_{HOO^-} is smaller by a factor of 10.7. These differences may arise from at least three factors: solvent effects on S$_N$2 displacement reactions may be large;[13] methods for calculating the necessary pK_a' values were different; there is a possible complication in 50% acetone from the formation of species such as 2,2-bis(hydroperoxy)propane.[14]

Aromatic Carbon.—Bigi and Pietra[15] report only a small α effect for the reaction of methoxylamine and of hydrazine[16] with 2,4-dinitrochlorobenzene. In view of the distinction between anionic and nonanionic α nucleophiles pointed out by Aubort and Hudson,[4b] we have examined the reaction of the anion of hydrogen peroxide with this substrate. We find k_{HOO^-} = 40 M^{-1} min^{-1} under the following conditions: 25°, [substrate] = 5×10^{-5} *M*, [H_2O_2] = 4.9–5.4 $\times 10^{-3}$ *M*, [EDTA] = 5×10^{-5} *M*, [NaOH] = 0.05–0.138 *M*, in 60% dioxane as solvent. The reaction was followed spectrophotometrically at 406 mμ, where 2,4-dinitrophenol has an extinction coefficient of 12,300 in this solvent. Bunnett and Davis[16] report that k_{HO^-} at 25° in this solvent is 0.066 M^{-1}min^{-1}. We confirm this value. Our value for k_{HOO^-} is 20 M^{-1} min^{-1} after the statistical correction and the ratio k_{HOO^-}/k_{HO^-} is thus 300. This represents a large α effect on the basis of this ratio, although the displacement of the point for HOO^- from the line defined by a series of primary *n*-alkylamines[15] is not large.

pK_a' Values for the Hydroperoxides.—Table VI compares our pK_a' values with literature values, corrected in each case to 25° and an ionic strength of 1.0. Since the reported values differ by as much as 0.2 p*K* units, we may expect that rate constants based on these ionization constants to differ by as much as a factor of 1.6.

Polarizability.—Ingold[4i] has suggested that there is a special factor of inhomogeneous polarizability associated with α nucleophiles which is important for

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TABLE VI

pK_a' VALUES OF HYDROPEROXIDES IN WATER, 25°, $\mu = 1.0$[a]

	pK_a'				
Hydroperoxide	E. & U.[b]	E. & M.[c]	S. & H.[d]	This study	ΔH_{ion}
HOOH	11.25	11.2	11.25	11.37[e]	8.9,[d] 7.0[e]
CH_3OOH		11.1		11.08[e]	6.5[e]
CH_3CH_2OOH		11.4	11.05		5.0[d]
i-C_3H_7OOH		11.7	11.45		7.5[d]
$(CH_3)_3COOH$		12.4	12.25	12.45[e]	7.1,[e] 6.4[d]

[a] Values from references *b*, *c*, and *d* are corrected to $\mu = 1.0$, 25° using the ionic strength correction term given by Evans and Uri,[b] $-0.5\,\mu^{1/2} + 0.08\,\mu$, and the ΔH_{ion} values given in the table. [b] M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949). [c] A. J. Everett and G. J. Minkoff, *ibid.*, **49**, 410 (1953). [d] W. F. Sager and J. C. Hoffsommer, *J. Phys. Chem.*, **73**, 4155 (1969). [e] This study: $\mu = 1.0$ with KCl at 25°. Our values at higher temperatures follow: HOOH at 39°, 11.15; MeOOH at 39°, 10.89; *tert*-BuOOH at 44.5°, 12.15. See also W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, **35**, 4012 (1970), who find ΔpK for HOOH and *tert*-BuOOH in 40% methanol = 1.25, in good agreement with the Δ values in water.

TABLE VII

Substrate	$\lvert\alpha\beta\rvert$	k_{HOO^-}/k_{HO^-}[a]
Ethyl acetate	0[b]	10^{-4}[b]
Bromoacetic acid	0.023[b]	13[f]
α-Bromo-*p*-toluic acid	(0.005)[c]	13[f]
p-Nitrophenyl methylphosphonate	0.26[d]	50[g]
p-Nitrophenylacetate	0.32[b]	77[f]
2,4-Dinitrochlorobenzene	0.52[e]	300[h]

[a] The ratios are temperature dependent. See Tables I–V. [b] Data of Klopman, *et al.*,[4a] $\alpha = 0$, $\beta = 0.8$ (ethyl acetate); $\alpha = 2.1$, $\beta = -0.011$ (bromoacetate); $\alpha = 0.7$, $\beta = 0.46$ (*p*-nitrophenylacetate). [c] Data of Klopman, *et al.*,[4a] for benzyl bromide, $\alpha = 2.5$, $\beta = 0.002$. [d] Data of Behrman, *et al.*,[9] using the points at 60° for N_2H_4, NH_2O^-, pyridine, PhO^-, and HO^-. $\alpha = 1.5$, $\beta = 0.17$. [e] References 15 and 16 using the points for PhS^-, $PhNH_2$, N_2H_4, NH_3, and HO^-. k_{H_2O} was estimated as $7.8 \times 10^{-12}\ M^{-1}$, sec^{-1}, 40° from the data of J. Murto, *Acta Chem. Scand.*, **18**, 1043 (1964), for 2,4-dinitrofluorobenzene on the assumption that k_{HO^-}/k_{H_2O} for the two substrates and for the temperature range 25–40° do not differ significantly. $\alpha = 3.5$, $\beta = 0.15$. [f] Our data, see Tables I–III. [g] Data of Behrman, *et al.*,[9] 30°. [h] Our data in 60% dioxane–water. NOTE ADDED IN PROOF.—J. E. Dixon and T. C. Bruice [*J. Amer. Chem. Soc.*, **93**, 6592 (1971)] have reported that k_{HOO^-}/k_{HO^-} for 2,4-dinitrochlorobenzene in water at 30° is 3.9×10^4. We have redetermined our data for this substrate in water at 25° with the other conditions substantially the same as those used for 60% dioxane (this table). We find $k_{HO^-} = 8.5 \times 10^{-3}\ M^{-1}$ min^{-1} and $k_{HOO^-} = 6.35\ M^{-1}$ min^{-1} (statistically corrected). Our ratio in water is thus 750. We do not know how to account for this large discrepancy. We have considered the possibility of the fast formation of the 2,4-dinitrophenyl peroxide anion followed by the slow formation of the phenoxide, but we exclude this since we observe no rapid formation of chloride ions. We have also considered the fast formation of an intermediate of the cyclohexadienone type [L. G. Cannell, *ibid.*, **79**, 2927, 2932 (1957)] which we also exclude since we observe no rapid change in the spectra of reaction mixtures in the region around 280 nm.

their reactivity. Since even inhomogeneous polarizability should provide a component of extra polarizability in the average direction, we have measured approximate values (±5%)[17] for the molar refractions of the anions of hydrogen peroxide and of methyl hydroperoxide at 25°, 589 mμ. We find the following increases in $[R]_D$ for the anions as compared with the undissociated species: H_2O, 1.05;[18] H_2O_2, 0.86; MeOOH, 0.93 (cc mol^{-1}). We do not therefore observe any extraordinary polarizability of these anions within the error limits of our measurements. See also ref 4j.

α-Effect Correlations.—Ibne-Rasa and Edwards[19] first suggested that the α effect might arise from ground-state destabilization due to electrostatic repulsion between the adjacent electron pairs on the reacting atom and the α atom. These arguments have been refined recently.[4a,b,i] In particular, Aubort and Hudson[4b] have proposed that "a positive α effect is produced by a decrease in the overlap integral of orbitals containing lone pairs of electrons in the course of a chemical reaction" and that the magnitude of the effect is governed by the conformation of the nucleophile. They further suggest that it is only the anionic α nucleophiles such as ROO^-, ClO^-, RSS^-, and certain *N*-methylhydroxamic acids whose α effect is due to p_π–p_π overlap. These α nucleophiles should therefore exhibit enhanced reactivity toward all substrates in contrast to nucleophiles such as hydrazine and hydroxylamine, whose special reactivity they attribute to other causes. One must make clear one's definition of the α effect. Edwards and Pearson[3] spoke of the enhanced reactivity of α nucleophiles as a reactivity which could not be accounted for by basicity and polarizability, *i.e.*, those nucleophiles whose reactivity deviated from the line defined by the Edwards equation:[20] $\log k/k_0 = \alpha E_n + \beta H$. Others have, in effect, redefined the α effect as situations in which the rate ratio k_{HOO^-}/k_{HO^-} is large (a definition which may suffer from abnormally low values for k_{HO^-}), or as cases in which the reactivity cannot be accounted for by basicity alone, *i.e.*, as a deviation from a Brønsted plot. For the case of HOO^-, we find an enhanced reactivity for all substrates whichever of these bases we use.[21] This is not true for hydrazine and hydroxylamine. Gregory and Bruice[4e] find no enhanced reactivity for hydrazine, hydroxylamine, or methoxylamine in reactions with methyl iodide as measured by displacement from a Brønsted plot of primary amines. This is consistent with the ideas of Aubort and Hudson[4b] as already discussed. On the other hand, Pearson, *et al.*,[22a] find $k_{N_2H_4}/k_{NH_3} \cong 10$ toward methyl iodide as a substrate and Klopman, *et al.*,[4a] view evidence of this sort as an indication of an α effect. Klopman, *et al.*,[4a] have reexamined the application of the Edwards equation to the prediction of enhanced reactivity of α nucleophiles. They have made the qualitative suggestion that in order for the α nucleophile to exhibit enhanced reactivity with a particular substrate, the ratio of the Edwards coefficients, α/β, must be large and at the same time, β must be sizable. In examining their data and our own results, we have observed what appears to be a quantitative correlation, namely that a plot of $\log (k_{HOO^-}/k_{HO^-})$ *vs.* $\lvert\alpha\beta\rvert$ is linear. The data we have used for this correlation are shown in Table VII.[22b] The oxibase

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[17] Judged from the correspondence between our value for H_2O_2 and those given by W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide," Reinhold, New York, N. Y., 1955, p 271.

[18] R. J. W. LeFèvre, *Advan. Phys. Org. Chem.*, **3**, 23 (1965).

[19] K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962).

[20] J. O. Edwards, *ibid.*, **76**, 1540 (1954). See also K. M. Ibne-Rasa, *J. Chem. Educ.*, **44**, 89 (1967). Also known as the oxibase scale.

[21] We have used our value for the molar refraction of HOO^-, 6.7 cc mol^{-1}, to calculate 1.76 V as the E_n value for HOO^-. See J. O. Edwards, *J. Amer. Chem. Soc.*, **78**, 1819 (1956), and K. M. Ibne-Rasa, *J. Chem. Educ.*, **44**, 89 (1967).

[22] (a) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968). (b) A reviewer has suggested that coupling between the αE and βH terms would give rise to a cross term with the coefficient $\alpha\beta$. See the discussion in J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 139–146.

scale plots were each drawn so as to include the point for HO^-. There is considerable scatter in the plots and so somewhat different values for α and β could have been used. Nevertheless, we feel that the trend toward the correlation we have used is there. This observation is consistent with the view[4a] that both the αE_n and the βH terms in the Edwards oxibase scale equation are important for the existence of α nucleophilicity. We note that our data show an increase in the ratio k_{HOO^-}/k_{HO^-} in the progression from sp^3 to sp^2 to sp carbon. This is, in part, fortuitous, since ethyl acetate is not attacked at a significant rate by HOO^-.[23]

Experimental Section

Substrates and Nucleophiles.—α-Bromo-*p*-toluic acid was prepared from α-chloro-*p*-tolunitrile (Matheson Coleman and Bell) by a modification of the method of Exner and Jonas.[24] Excess HBr was removed from the crude product under vacuum rather than by reprecipitation from 10% sodium carbonate solution, since this latter procedure in our hands yielded only α-hydroxy-*p*-toluic acid. The yield of α-bromo-*p*-toluic acid, mp 230–231° (corrected), was *ca.* 100%. *Anal.* Calcd: Br, 37.19. Found: Br, 37.40 (Galbraith Laboratories).

Bromoacetic acid and *p*-nitrophenyl acetate were Eastman products. The latter was recrystallized from hexane, mp 77–78° (corrected).

p-Nitrophenyl sulfate was obtained from the Sigma Chemical Co. It contained about 1% free *p*-nitrophenol and was used without recrystallization.

p-Cyanobenzoic acid (Aldrich Chemical Co.) was recrystallized twice from deionized water following an initial purification by extraction of an impurity with ether from aqueous buffer, pH 6.5, and treatment with charcoal.

tert-Butyl hydroperoxide (Matheson, Coleman, and Bell) was distilled under vacuum before use. Methyl hydroperoxide was prepared by a modification[9] of the original procedure of Rieche and Hitz.[25] *p*-Nitroperoxybenzoic acid and *p*-methoxyperoxybenzoic acid were prepared by the method of Vilkas.[26] *m*-Chloroperoxybenzoic acid and peroxyacetic acid were obtained from the Aldrich Chemical Co. and the FMC Corp., respectively.

Kinetics.—Second-order rate constants were obtained either by division of the corrected k_0 values by the calculated concentration of the anionic nucleophile and by the concentration of the substrate or by division of the corrected k_ψ values by the calculated concentration of the anionic nucleophile. The reported second-order rate constants for hydrogen peroxide have been divided by two for the statistical correction.

The reactions of bromoacetic acid and of α-bromo-*p*-toluic acid with nucleophiles were followed by measurement of the increase in bromide ion concentration with time. For the reactions with the hydroperoxides and with hydroxide ion, reaction aliquots were quenched with acetic acid and then titrated with standard silver nitrate solutions. The end point was detected using an Orion bromide-specific electrode. The bromide electrode was found to respond erratically in the presence of peroxycarboxylic acids. Therefore, for these nucleophiles, the peroxy acids were first rapidly[27] reduced by a cold 0.01 *M* methionine-acetic acid mixture followed by the silver nitrate titration at room temperature.

The reactions of *p*-nitrophenyl acetate and of *p*-nitrophenyl sulfate were followed by measurement of the rate of increase of *p*-nitrophenoxide ion concentration at 407 mμ using a Perkin-Elmer model 202 recording spectrophotometer equipped with a thermostatted cell compartment. Both zero- and first-order conditions were used. Division of the pseudo-first-order rate constant by the nucleophile concentration gave second-order constants in good agreement with those obtained by the pseudo-zero-order technique. When necessary, suitable corrections were made for the buffer rate and the water rate. The concentration of *p*-nitrophenoxide anion was calculated for a particular pH and temperature using the value $pK_a' = 7.15$ at 25°,[28] and an experimentally determined heat of ionization at $\mu = 1.0$ of 3300 cal/mol in the range 25–54°. This value was determined by measurement of the absorbance of a solution of *p*-nitrophenol at constant pH as a function of temperature.

The reaction of *p*-cyanobenzoic acid with hydroxide ions was followed by the decrease in the absorbance at 235 mμ. The ratio of the extinction coefficients $\epsilon_{\text{nitrile}}/\epsilon_{\text{amide}}$ at this wavelength is 1.23. The reaction of *p*-cyanobenzoic acid with hydrogen peroxide was followed by measurement of the decrease in hydrogen peroxide concentration. When stoichiometric concentrations of nitrile and hydrogen peroxide were used, plots of $2/[H_2O_2]$ *vs.* time were linear. The slope of this plot is $2k_{HOO^-}K_a/[H^+]$. k_{HOO^-} values calculated from these plots agreed well with values derived from pseudo-first-order plots with $[H_2O_2]$ limiting.

For nucleophiles ionizing in the pH range of the experiment, the concentration of the anion was calculated from the pK'_a values given in the Tables. pK'_a values for the peroxycarboxylic acids at an ionic strength of 1.0 (KCl) were measured potentiometrically. The values are consistent with those given by Goodman, *et al.*[29]

pK'_a Values for the Hydroperoxides. A. *tert*-Butyl Hydroperoxide.—A Beckman Research pH meter equipped with a 0–14 Corning combination electrode was used. The system was standardized at pH 10.0, 25° (borate buffer) and at pH 12.45, 25° (saturated calcium hydroxide).[30] The absorbancy of 0.01505 *M* *tert*-butyl hydroperoxide was measured at 270 mμ after the addition of various amounts of sodium hydroxide solutions. The ionic strength was maintained at 1 by the addition of KCl. The molar absorbancy of *tert*-butyl hydroperoxide anion at 270 mμ was 61.7 cm^{-1} and that of the un-ionized molecule 6.85 cm^{-1}. The pH and the absorbance of the solutions at 270 mμ were then measured at four pH values, at both 25 and 44°.

B. Hydrogen Peroxide and Methyl Hydroperoxide.—The pK_a' values for these peroxides were determined potentiometrically at an ionic strength of 1.0 (KCl) using the same setup as described for *tert*-butyl hydroperoxide. Eight to ten additions of sodium hydroxide solution were made, after which the pH was determined at both 25 and 39°. pK_a' values were calculated, making corrections for the hydroxide ion concentration as outlined by Albert and Serjeant.[28] K_w values at $\mu = 1.0$ are 1×10^{-14} at 25° and 2.8×10^{-14} at 39°.[31]

Activation Parameters.—Apparent E_a values were obtained from slopes of the plots of the apparent second-order rate constants against the reciprocal of temperature. For the hydroperoxides, the apparent second-order rate constants were calculated using the pK_a' values for 25°. Actual E_a values were obtained by subtraction of the heats of ionization for the hydroperoxides from the apparent E_a. We estimate that the values for E_a and hence for $\Delta H^{\ddagger}$ are no better than ± 1 kcal/mol and that the $\Delta S^{\ddagger}$ values are no better than ± 3 cal mol^{-1} deg^{-1}.

Registry No.—α-Bromo-*p*-toluic acid, 6232-88-8; bromoacetic acid, 79-08-3; *p*-nitrophenyl acetate, 830-03-5; *p*-nitrophenyl sulfate, 1080-04-2; *p*-cyanobenzoic acid, 619-65-8.

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