

Nucleophilic Reactivities of Bleach Reagents

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S Supporting Information

ABSTRACT: The nucleophilicities of the oxidants hydroperoxide, hypochlorite, hypobromite, bromite, and peroxymonosulfate were determined by following the kinetics of their reactions with a series of benzhydrylium ions of known electrophilicity (E) in alkaline, aqueous solutions at 20 °C. The reactivities of the oxidants correlate only weakly with their basicities. Analyzing the rate constants by using the relationship log $k_2 = s_N(N + E)$ gave the



parameters N (and s_N), which were applied to predict the rates of Weitz-Scheffer epoxidations.

ydrogen peroxide, hypochlorite, or persulfates are low-cost oxygen-nucleophiles and are often the oxidants of choice for industrial applications. They are used for the transfer of oxygen atoms in organic synthesis¹ and also at large scale for the bleaching of paper pulp and textiles, in disinfectants, or as ingredients in cosmetics.² It is generally recognized that the hydroperoxide anion, hypochlorite, or persulfate are nucleophilic species that undergo analogous reactions with organic electrophiles. Although several of these reactions had been studied kinetically³ and reactions of bleach reagents with cationic organic food dyes are used in tutorials for introducing kinetic methods to students,⁴ a direct comparison of reactivities of different oxygen-transfer reagents is not available to date.

We now set out to investigate the nucleophilic reactivity of the hydroperoxide anion (1, originating from H_2O_2 -urea, H₂O₂-polyvinylpyrrolidone, or H₂O₂-sodium carbonate complexes), hypochlorite (2), hypobromite (3), peroxymonosulfate (4), and bromite (5) in alkaline, aqueous solution by following the kinetics of their reactions with the benzhydrylium ions 6a-6e as reference electrophiles (Figure 1). The second-order rate constants $k_2(20 \text{ °C})$ of these reactions and the known electrophilicities E of $6a-6e^5$ were then applied in the linear free-energy relationship (see eq 1)⁶ to derive the nucleophilicity parameters N and the susceptibilities s_N of the oxidants 1–5.

$$\log k_2(20^{\circ}\mathrm{C}) = s_{\mathrm{N}}(N+E) \tag{1}$$

Thus, the anionic oxygen nucleophiles studied in this work can be integrated into Mayr's comprehensive nucleophilicity scale,⁷ which enables the direct comparison of the nucleophiles 1-5 with previously investigated organic peroxide anions⁸ and more than 1000 other nucleophilic species whose reactivities were investigated by the benzhydrylium method.⁶⁰

We observed that the decoloration of the deeply blue aqueous solution of 6a upon treatment with an alkaline solution of hydrogen peroxide (2 equiv $H_2O_2\text{, from }\textbf{1}_{UHP})$ was accompanied by the formation of a colorless precipitate. Concentration of a dichloromethane extract of the reaction mixture yielded colorless needles (mp 137 °C), which were analyzed by single-crystal X-ray diffraction (XRD). Instead of the expected 1:1-adduct, benzhydryl hydroperoxide 7, the



Figure 1. Nucleophiles and reference electrophiles included in this study. Electrophilicity (E) values are taken from ref 5.

bis(benzhydryl)peroxide 8 was detected, which can be rationalized by the subsequent reaction of the initially formed benzhydryl hydroperoxide 7 with a second equivalent of 6a. Isolating the precipitate by filtration of the aqueous reaction mixture gave 8 in a yield of 58% (see Scheme 1).

As in the solid-state structure of bis(triphenylmethyl)peroxide,^{9,10} 8 has a center of inversion in its crystal structure and a C-O-O-C dihedral angle of 180°. Steric bulk around the COOC units is compensated differently in 8 and Ph₃COOCPh₃, however: bis(triphenylmethyl)peroxide has a "normal" O–O bond length (148.0 pm), 9,11 but elongated C– O (146.1 pm) and C–C_{ar} distances (153.3 pm). In contrast, the solid-state structure of 8 is characterized by normal C-O (140.6 pm) and $C-C_{ar}$ bond lengths (152.5 pm), but an unusually long O-O bond (151.3 pm), which is significantly longer than the usually observed O-O bond lengths in other dialkyl peroxides (145-146 pm).^{10,11} Packing effects may

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Scheme 1. Bis(benzhydryl)peroxide 8 from the Reaction of 6a with Hydrogen Peroxide in Alkaline Solution



^aMolecular structure of 8 in the crystal (thermal ellipsoids are drawn at a 50% probability level at T = 100 K).

account for these structural differences, because the solid-state structure of **8** shows motifs of intermolecular $\pi - \pi$ stacking, which are not found in the crystal structure of bis-(triphenylmethyl)peroxide [see the Supporting Information (SI)].

The kinetics of the reactions of 1-5 with the benzhydrylium ions 6b-6e as reference electrophiles were measured in alkaline, aqueous solution by using the previously established procedure (see Figure 2).^{8,12} In all kinetic experiments,



Figure 2. (A) Reaction of benzhydrylium ions 6 with nucleophiles in alkaline, aqueous solution of bleach reagents XOH. (B) Absorbance A (at 610 nm) vs time for the reaction of $\mathbf{1}_{\text{UHP}}$ ($c = 2.46 \times 10^{-4}$ M) with 6b ($c = 1.05 \times 10^{-5}$ M) at 20 °C. (C) The slope of the linear plot of the first-order rate constant k_1 (= $k_{\text{obs}} - k_{\text{OH}}$ [HO⁻]) versus nucleophile concentration was used to derive the second-order rate constant k_2 for the attack of the anion 1 at the benzhydrylium ion 6b.

acetonitrile [<0.5% (v/v)] was used as a co-solvent to solubilize the benzhydrylium tetrafluoroborates. Applying a high excess of the anions 1-5 over the electrophiles **6b**-**6e** caused the nucleophile concentrations to remain almost constant during the kinetic runs. As $[1]_0 \gg [6]_0$, electrophiles **6** were quantitatively consumed by the excess of HOO⁻ ions under the conditions of the kinetic experiments, and the subsequent reaction of 7 with **6** could be neglected in the kinetic analysis. We followed the progress of the reactions by time-resolved stopped-flow UV/vis photometry, which showed a monoexponential decay of the absorption of the electrophile in all investigated reactions (Figure 2B). First-order rate constants k_{obs} (s⁻¹) were obtained from least-squares fitting of the singleexponential function $A_t = A_0 \exp(-k_{obs}t) + C$ to the decaying absorbances.

As expressed by eq 2 and Figure 2, the observed first-order rate constants k_{obs} reflect the reactions of cations 6 with water, hydroxide ions (HO⁻), and the anions of the bleach reagents (XO⁻).

$$k_{\rm obs} = k_{\rm W} + k_{\rm OH} [{\rm HO}^-] + k_2 [{\rm XO}^-]$$
 (2)

The basicities of the investigated anions $(pK_{aH} \text{ in Table } 1)^{13}$ were used to calculate the concentrations [OH⁻] and [XO⁻]. Rate constants for the reactions of the cations 6a-6e with water $(k_{\rm W})$ and hydroxide ions $(k_{\rm OH})$ had previously been reported.^{3h} Thus, the second-order rate constants k_2 (Table 1) for the attack of the nucleophiles 1-5 at the benzhydrylium ions 6b-6e were obtained from the slopes of the linear correlations of k_1 (= $k_{obs} - k_{OH}$ [HO⁻]) with the nucleophile concentrations (Figure 2C). Table 1 lists the nucleophilicity parameters for 1 (generated from different H_2O_2 formulations), along with the N and s_N values for anions 2-5. The linear correlations of the second-order rate constants k_2 with the electrophilicity E of the benzhydrylium ions (Figure 3) furnished the nucleophilicity parameter N of the anions 1-5as the intercept with the abscissa (equal to -E at log $k_2 = 0$). The individual susceptibilities of the nucleophiles toward changes in the electrophiles' reactivity are reflected by the different slopes (s_N) of the log k_2 vs E correlations.

Table 1 shows that the nucleophilic reactivity of HOO⁻ (1) toward the reference electrophiles **6** is almost independent of the source of the reactant: hydrogen peroxide anions liberated from H_2O_2 -urea (UHP), H_2O_2 -polyvinylpyrrolidone (PVP), or sodium percarbonate (SPC) are only slightly less reactive than HOO⁻ generated from aqueous hydrogen peroxide, for which N = 15.40 ($s_N = 0.55$) was reported in ref 3h.

Bromite (BrO₂⁻, **5**) is significantly less reactive than hypobromite (BrO⁻, **3**). Depending on the electrophilic reaction partner, the rate constants for the reactions of **6** with **5** are lower by a factor 10–20 than the k_2 values for the reactivities thus follow the order of basicities because BrO₂⁻ ($pK_{aH} = 3.43$) is a weaker base than BrO⁻ ($pK_{aH} = 8.8$). In contrast, the reactivities of **1**–4 toward electrophile **6c** (Table 1) are almost identical, although their basicities (pK_{aH}) differ by 4 orders of magnitude.¹⁴ Figure 4 is, thereby, giving another example for the fact that the Brønsted basicities cannot be used as a guideline for predicting the reactivities of nucleophiles, even when the reacting atom remains the same as in the bleach reagents XO⁻.

How can the weak correlation of basicity and reactivity ($r^2 = 0.4614$) in the series HOO⁻, ClO⁻, BrO⁻, [SO₅]²⁻ be explained? It has recently been shown that early transition states in reactions of the anions of organic peroxides ROO⁻ with benzhydrylium ions put desolvation of the nucleophile into a key position for understanding the counterintuitive nucleophilicity ordering.⁸ It is likely that analogous solvation effects also control the nucleophilic reactivities of anions 1–4 in aqueous solution.¹⁵

To assess the applicability of N and s_N of 1–5, we next studied the kinetics of the reactions of Malachite Green (MG) with 1, 2, and hydroxide (see Table 2). The second-order rate constants that we determined experimentally agreed within a factor of 10 with those predicted by applying eq 1, the electrophilicity parameter for MG (E = -10.29, from ref 3h), and the nucleophile-dependent parameters N and s_N from

Table 1. Basicities (pK_{aH}) and Second-Order Rate Constants k_2 for the Reactions of the Nucleophiles 1–5 with Reference Electrophiles 6a–6e in Alkaline, Aqueous Solution at 20 °C

		$k_2 (M^{-1} s^{-1})$				
XO ⁻	pK_{aH}^{a}	6e	6d	6c	6b	$N(s_{\rm N})$
1_{UHP}	11.75	8.18×10^{2}	1.28×10^{3}	3.89×10^{3}	1.49×10^{4}	15.20 (0.55)
1_{PVP}	11.75	6.94×10^{2}	1.11×10^{3}	3.23×10^{3}	1.45×10^{4}	14.86 (0.58)
1 _{SPC}	11.75	6.84×10^{2}	1.00×10^{3}	2.96×10^{3}	1.15×10^{4}	15.16 (0.54)
2	7.53	5.00×10^{2}	6.71×10^{2}	2.03×10^{3}	1.03×10^{4}	14.50 (0.58)
3	8.8	1.09×10^{3}	1.94×10^{3}	4.05×10^{3}	1.27×10^{4}	16.69 (0.46)
4	9.4	5.01×10^{2}	6.53×10^{2}	2.79×10^{3}	1.06×10^{4}	14.41 (0.60)
5	3.43	4.67×10^{1}	6.63×10^{1}	2.72×10^{2}	9.71×10^{2}	12.75 (0.59)
D · · · · 77	· 1 C	6.12				

^{*a*}Basicities pK_{aH} are taken from ref 13.



Figure 3. Plot of log k_2 (Table 1) for the reactions of anions 1_{UHP} , 2, 3, and 5 with electrophiles **6b–6e** in alkaline aqueous solution at 20 °C versus the electrophilicity parameters *E* of **6b–6e** (see the SI for individual plots for all nucleophiles).



Figure 4. Correlation of the reactivities of the nucleophiles 1-5 (toward **6c**) with their basicities (pK_{aH}) .

Table 2. Second-Order Rate Constants k_2 for the Reactions of MG with Nucleophiles in Aqueous Solution (at 20 °C)

	Rate Constants (M ⁻¹ s ⁻¹)				
XO ⁻	$k_2^{ m thiswork}$	$k_2^{\text{calcd } a}$	$k_2^{ m lit}$		
HO ⁻	9.25×10^{-1}	1.25	2.18 $(25 \ ^{\circ}C)^{b}$		
$HOO^{-}(1)$	1.13×10^{3}	6.46×10^{2}	$1.3 \times 10^4 (30 \ ^\circ \text{C})^c$		
$ClO^{-}(2)$	2.59×10^{3}	2.76×10^{2}	$5.0 \times 10^1 (30 \ ^{\circ}\text{C})^c$		
			$1.0 \times 10^3 (23 \ ^{\circ}\text{C})^d$		

^{*a*}Calculated based on eq 1, the electrophilicity of MG (E = -10.29, from ref 3d) and the N (and s_N) parameters in Table 1 (for 1, 2) and ref 3d (for OH⁻). ^{*b*}Data taken from ref 16. ^{*c*}Data taken from ref 3c. ^{*d*}Data taken from ref 3d.

Table 1. The significantly lower reactivity of $\text{ClO}^-(2)$ toward MG, compared to HOO⁻(1), described by Dixon and Bruice,^{3c} was not observed in our measurements, which agreed better with Ritchie's data.^{3d}

Scheffer-Weitz epoxidations of arylidenemalononitriles (9) with various oxygen-transfer reagents had been described previously.^{8,17} We used these reactions to test whether the nucleophilicity parameters N (and s_N) for 1–5 (Table 1) also hold for the reactions of 1–5 with neutral electrophiles and, therefore, determined the rate constants for the nucleophilic epoxidations of 9a–9c (see Table 3).

Table 3. Second-Order Rate Constants k_2 for the Reactions of the Oxygen Nucleophiles 1–5 with the Neutral Electrophiles 9a–c in Alkaline, Aqueous Solution at 20 °C



Y = H: **a**; Y = OMe: **b**; Y = NMe₂: **c**

		Rate Constants (M ⁻¹ s ⁻¹)			
nucleophile	9 (E) ^a	k_2^{\exp}	$k_2^{\text{calcd } b}$	$k_2^{\rm exp}/k_2^{ m calcd}$	
$HOO^{-}(1_{UHP})$	9a (-9.42)	3.92×10^{4}	1.51×10^{3}	26	
	9b (-10.80)	7.97×10^{3}	2.63×10^{2}	30	
	9c (-13.30)	4.25×10^{2}	1.11×10^{1}	38	
$ClO^{-}(2)$	9a (-9.42)	6.63×10^{3}	8.84×10^{2}	7.5	
	9b (-10.80)	1.39×10^{3}	1.40×10^{2}	9.9	
BrO ⁻ (3)	9 a (-9.42)	1.10×10^{4}	2.21×10^{3}	5.0	
	9b (-10.80)	2.40×10^{3}	5.12×10^{2}	4.7	
$[SO_5]^{2-}(4)$	9 a (-9.42)	7.99×10^{3}	9.86×10^{2}	5.4	
	9b (-10.80)	1.49×10^{3}	1.47×10^{2}	10	
$BrO_{2}^{-}(5)$	9a (-9.42)	2.91×10^{1}	9.35×10^{1}	0.31	
^{<i>a</i>} Electrophilicitie applying eq 1, E	es E from ref 18 of 9 (this table)	8. ^b Second-or and N and s _N	der rate cons of 1–5 (from	tant k_2 by Table 1).	

Table 3 shows that the predicted rate constants (k_2^{calcd}) for the epoxidations of the electron-deficient π -systems of 9 with the nucleophiles 2–5 match the experimentally obtained rate constants (k_2^{exp}) with a maximum deviation of a factor of 10, in the case of the hydroperoxide anion ($\mathbf{1}_{\text{UHP}}$) within a factor of 40. Hence, all determined rate constants for the epoxidations of 9 by 1–5 are within the usual prediction accuracy of eq 1 (that is, an error in the predicted rate constant within a factor of 10– 100).^{6b,c} For 2–5, the small deviations between measured (reactions with 9a and 9b) and predicted rate constants (based on reactions with benzhydrylium ions 6) suggest that analogous reaction mechanisms are operating, in which the first C–O bond formation between nucleophile and electrophile (e.g., the formation of 10) is rate-determining.

Because of the different susceptibility of BrO⁻ (3, $s_N = 0.46$), the relative reactivity of 3, if compared with other oxidants in Figure 5, will be dependent on the choice of the electrophile.



Figure 5. Comparison of nucleophilicity parameters *N* of anions 1-5 with those of other peroxide anions (from ref 8). [Superscript "*a*" denotes data taken from ref 3h.]

However, because of the comparable s_N values (0.54–0.60), a rough comparison of the reactivities of anions 1, 2, 4, and 5 with those of other anionic oxidants can be based solely on the nucleophilicity parameter *N*. Hence, Figure 5 shows that the anions 1, 2, and 4 are marginally more nucleophilic than the alkyl peroxide anions and less nucleophilic than various peroxybenzoates.⁸

In conclusion, the reactivity parameters of the oxidants 1-5 (in H₂O) derived in this work from the rates of their reactions with benzhydrylium ions may be used for the design of oxygentransfer reactions toward various types of C-centered electrophiles (e.g., Michael acceptors).¹⁹ The comparable reactivities of 1, 2, and 4 may be of interest for practical applications: interchanging these bleach reagents will not change the resulting reactivity. Only the pH of the solution must be adjusted, since alkaline conditions are required to generate the anions 1 and 4, while hypochlorite (2) is significantly deprotonated even under neutral conditions. Furthermore, the collection of reactivity data in this work and in ref 8 provides a unique foundation for a future re-evaluation of the α -effect in oxygen nucleophiles.²⁰

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b00645.

Synthetic procedures, analytical data, X-ray structure determinations, details of the kinetic measurements, and copies of NMR spectra (PDF)

Accession Codes

CCDC 1819620–1819621 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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