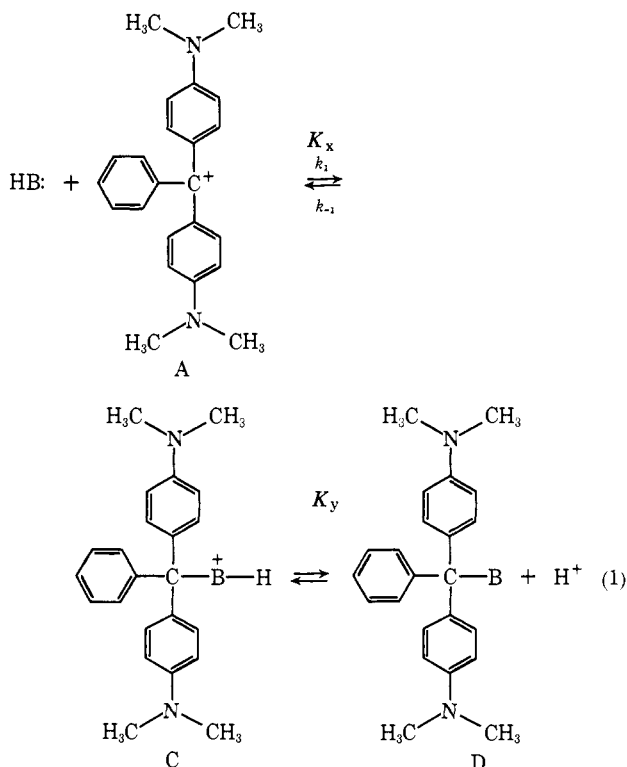# α Effect. IV. Additional Observation on the α Effect Employing Malachite Green as Substrate

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Contribution from the University of California at Santa Barbara, Santa Barbara, California. Received November 4, 1970

Abstract: The values of $\Delta F^{\pm}$ and ΔF° for the reaction of HOO^- and other assorted α-effect nucleophiles with malachite green have been determined. The results of this study are compared to those of a previous investigation of the reaction of hydrazines with malachite green. For the latter reactions, comparisons of rate and equilibrium data for hydrazines and amines of the same pK_a established that a decrease in $\Delta F^{\pm}$ associated with the α effect was quantitatively reflected in a more negative ΔF°. For the nucleophiles ClO^- and HOO^-, ΔF° is again greater than anticipated from the pK_a; however, in these cases the decrease in $\Delta F^{\pm}$ is much greater than can be explained through enhanced stability of the addition products. The possibility that polarizability is responsible for the unusual reactivity of HOO^- has been explored *via* the Bunnett technique of employing 2,4-dinitrohalobenzenes as substrates. The magnitude of the α effect may be expressed as the ratio of rate constants for a hydrazine and an amine of like basicity (*e.g.*, $k^{N_2H_4}/k^{glycylglycine}$). A relationship apparently exists between the α effect and the Brønsted β value for the nucleophilic reaction of amines with a series of substrates with decrease in the α effect accompanying decrease in β. A similar correlation does not seem to hold for oxyanions and HOO^-. The reactions of both amines and oxyanions with methyl tosylate are characterized by small values of β (≈ 0.2) which presumably indicate little bond formation in the transition state. The reaction of hydrazines with methyl tosylate does not exhibit the α effect whereas HOO^- does—these conclusions being based on the lack of a positive deviation of hydrazines from a Brønsted plot for the primary amines and the observation of a positive deviation for HOO^- from the Brønsted plot for alkoxide ions. It must be concluded that factors leading to the kinetic α effect are varied and different in the case of hydrazines and peroxide ions.

The term α effect has been used to denote the high reactivity of nucleophiles possessing an unshared pair of electrons adjacent to the nucleophilic atom.[3] A previous paper from this laboratory[4] established that

$$HB: + A \underset{k_{-1}}{\overset{K_x, k_1}{\rightleftharpoons}}$$

the difference in the free energy of reaction between amines and hydrazines of like pK_a with malachite green (eq 1) is quantitatively the same as the difference in the standard free energy for the formation of the addition products. In the present study the relationship of $\Delta F^{\pm}$ to ΔF° and the position of the transition state as well as the role of polarizability are extended to the reaction of other α-effect nucleophiles, such as HOO^-, with malachite green.

Experimental Section

Materials. Potassium acetate (Baker), sodium bisulfite (Mallinckrodt), hydrogen peroxide (Mallinckrodt), and sodium hypochlorite (Matheson Coleman and Bell) were all used without further purification. Trifluoroethanol (Aldrich) was subjected to vpc and showed no observable impurities. Propargyl alcohol (Aldrich) was distilled before use. Hydroxylamine hydrochloride (Matheson Coleman and Bell), N-hydroxyphthalimide (Aldrich), and 5,5-dimethyl-1,3-cyclohexanenedione (Aldrich) were recrystallized before use. The 2,4-dinitrophenyl acetate employed was that from another study.[5] Methyl tosylate (Matheson Coleman and Bell) was recrystallized several times before use. All other compounds were obtained from a previous study.[4]

Hydrogen peroxide solutions were standardized by titration with permanganate which was in turn standardized with oxalic acid. The reactions of hydrogen peroxide anion were run in the presence of 10^{-3} *M* EDTA to retard decomposition. The rates of reaction between HOO^- and 2,4-dinitroiodobenzene were unobtainable due to oxidation of the iodide ion and numerous side reactions that took place. A slow rate of decomposition of HOO^- takes place even in the presence of EDTA at concentrations as high as those in the reaction with methyl tosylate.

Solutions of sodium hypochlorite were standardized by titration with thiosulfate solution using potassium iodide and sulfuric acid according to the method described by Kolthoff and Sandell.[6] Solutions of sodium hypochlorite underwent a reaction with malachite green at pH values near 7; however, at higher pH values, 10.5–11.0, no observable changes in the dye took place.

$$C \underset{}{\overset{K_y}{\rightleftharpoons}} D + H^+ \quad (1)$$

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(1) A portion of this material to be submitted by J. E. D. in fulfillment of the requirement for the Ph.D. in Chemistry, University of California at Santa Barbara.

(2) To whom inquiries should be addressed.

(3) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

(4) J. E. Dixon and T. C. Bruice, *ibid.*, **93**, 3248 (1971).

(5) T. C. Bruice and A. Turner, *ibid.*, **92**, 3422 (1970).

(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Company, New York, N. Y., 1952, p 597.

Apparatus. Kinetic measurements were made with a Gilford Model 2000 or Zeiss PMQ II spectrophotometer. The Zeiss was equipped with a thermostated brass cuvette holder and the Gilford with dual thermospacers through which water circulated at the appropriate temperatures.

The pH of a kinetic solution was determined both prior to and at the completion of the reaction, using a Radiometer Model 22 pH meter with a PHA 630 scale expander, and a combined glass calomel electrode (Radiometer CK 2021 C) thermostated at 25° or 30 ± 0.1°.

All calculations of rate and equilibrium constants were performed on either an Olivetti-Underwood Programma 101 or a Hewlett Packard 9100A calculator using a least-squares fit in plots of k_{obsd} vs. $[B_T]$. A micropipet (Ependorf) was used to deliver stock solutions in both rate and equilibrium determinations.

Kinetics. Doubly glass distilled water was used to prepare all solutions, and serial dilutions were made with 1.0 M potassium chloride, to maintain ionic strength at 1.0. The temperature employed for all rate and equilibrium studies, save reactions in which 2,4-dinitrophenyl acetate was used as substrate, was 30 ± 0.1° while for the latter case the temperature was 25 ± 0.1°. All solutions were used on the same day that they were made up. All rate constants were determined under conditions where the concentration of the nucleophile was in large excess over that of the substrate, so that pseudo-first-order kinetics were obtained in all cases. Reactions were followed to completion, and rate constants were calculated from plots of log ($OD_\infty - OD_t$) vs. time.

The reactions of all amines and hydrazines with 2,4-dinitrophenyl acetate were followed at 370 nm. In all cases the amine–amine hydrochloride served as buffer. At least five buffer dilutions at three different pH values were performed for each amine or hydrazine. All reactions were found to be first order in amine or hydrazine.

The rates of reaction with amines and hydrogen peroxide anion, etc., with malachite green were followed by a loss in absorption of substrate at 620–625 nm. The details of these measurements have previously been described.[4]

The appearance of 2,4-dinitrophenol was followed at 370 nm and that of 2,4-dinitroperoxide anion at 340–360 nm when either 2,4-dinitrofluorobenzene (DNFB) or 2,4-dinitrochlorobenzene (DNClB) were used as substrate. The rates of reaction with DNFB are rapid enough that decomposition of HOO^- or the resulting product is of little consequence whereas the slower rates observed for DNClB are complicated by decomposition. The presence of EDTA partially decreases the rates of H_2O_2 decomposition. Generally five serial buffer dilutions at three pH values were run to determine the rate constant for this reaction. The reactions of methyl tosylate with amines, hydrazines, oxyanions, and hydrogen peroxide anion were followed by monitoring a loss in absorption at 263–275 nm (depending upon the nucleophile employed). The amines plus their conjugate acids served as buffer. When alkoxides were employed as nucleophiles, the general procedure was to find a pH where the reaction of alkoxide exceeded that of hydroxide so that a buffer dilution could be used as a method of obtaining the second-order rate constants. Thus for nucleophiles such as the anion of propargyl alcohol it was necessary to obtain the rate constants where only a small quantity of alkoxide is present, for at higher pH values where more alkoxide is present the reaction is complicated by the competing reaction between HO^- and substrate. At extremely low concentrations of alkoxide ion no rate attributable to the anion could be obtained. No problems were encountered with the other alcohols studied. Several alcohols (chloral hydrate and pentaerythritol) could not be used because of their solubilities or their reactivities could not be observed over that of hydroxide. Substituted phenols were excluded because of their absorption in the region of 270–230 nm.

Equilibrium Determinations. The general approach for determination of the equilibrium constants with malachite green has been described previously.[4] The reactions of anions with malachite green afford values of K_x, whereas in attack by a neutral species both K_x and K_y values are obtained (eq 1). The determination of equilibrium constants with HOO^- and ClO^- is complicated by the fact that at higher concentrations no dye remains, whereas at lower concentrations the reaction of H_2O and HO^- compete with that of the nucleophile. Thus the values reported here are subject to considerable error (probably near one order of magnitude). No rate or equilibrium constants above those for H_2O or HO^- were noted for 5,5-dimethyl-1,3-cyclohexanedione.

Results

The pseudo-first-order rate constant (k_{obsd}) for disappearance of 2,4-dinitrophenyl acetate (2,4-DNPA) in aqueous solutions of amine buffers is related to the pH-dependent hydrolytic constant (k_0) and the second-order rate constant (k_2) for reaction of ester with amine free base (B:) via eq 2.[7] Values of k_2 (Table I) were

$$k_{obsd} = k_0 + k_2[B:] \qquad (2)$$

obtained as the slopes of plots of k_{obsd} vs. [B]. Pseudo-first-order rate constants were routinely obtained for each of five concentrations of amine buffer (B_T; where $[B_T] = [B:] + [BH]$) at each of three different pH values.
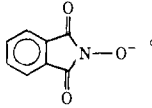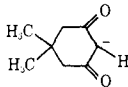
Table I. Second-Order Rate Constants for Reaction of Nucleophiles with 2,4-DNPA at 25° ($\mu = 1.0$ KCl)

Nucleophile	k_2, M^{-1} min^{-1}	pK_a
Hydrazine[a]	1.8×10^4	8.20
N,N-Dimethylhydrazine	1.1×10^3	7.56
Phenylhydrazine	70	5.27
Methoxylamine	27	4.78
Semicarbazide[a]	6.6	3.86
Acethydrazide	2.8	3.25
Thiosemicarbazide	0.048	1.75

[a] This value from ref 7.

Rate and equilibrium constants for nucleophilic addition to malachite green are provided in Table II.

Table II. Reaction of Nucleophiles with Malachite Green at 30° ($\mu = 1.0$ KCl When Not Specified)

Nucleophile	k_1, M^{-1} min^{-1}	K_x, M^{-1}	pK_a
MeO^{-a}	1.25×10^3	1.32×10^8	18.31
$^-$CN^b	41.4	1×10^6	9.14
HO$^-$	74	1.45×10^7	15.7
SO$_3^{2-}$	1.7×10^4		7.1
[phthalimide N—O$^-$][c]	1.4×10^2		6.1
HOO$^-$	8.0×10^5	$\cong 5.0 \times 10^7$	11.6
ClO$^-$	3.0×10^3	$\cong 3.0 \times 10^3$	7.1
[dimedone]	No reaction		5.2
H$_2$O^d	2.5×10^{-4}		-1.74
NH$_2$OH	5.4×10^2		6.17

[a] Value obtained in MeOH solution from C. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, **89**, 2063 (1967). [b] Value in H$_2$O from references in footnote a. [c] Reaction carried out in 20% dioxane, $\mu = 0.1$ with KCl. [d] Rate constant is given in units of min^{-1}.
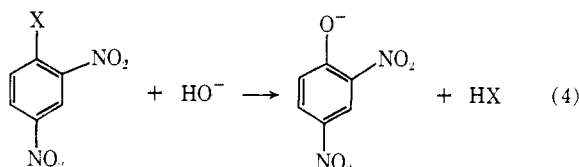
The kinetic rate expression takes the form of eq 3 at

$$k_{obsd} = k_0 + k_{OH}[HO^-] + k_1[B:] \qquad (3)$$

concentrations of nucleophile much greater than substrate (such that [B:] $\gg$ malachite green) where the addition of amine to malachite green proceeds to completion. Equilibrium constants are obtained by reducing the concentration of nucleophile so both [A]

(7) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90**, 2622 (1968).

and/or [C] and [D] are present; k_{-1} may then be obtained from K_x (see ref 4). The kinetic rate expression necessary for this purpose has been described in a previous paper from this laboratory.[4] The equilibrium constants for HOO^- and ClO^- are only approximate numbers because at extremely low concentrations of nucleophile both H_2O and HO^- compete for substrate. Thus, the general procedure was to employ concentrations of nucleophiles so that reaction was rapid enough not to be subject to interference by lyates. No statistical corrections have been applied to any nucleophile possessing a pair of α-electrons. Examples are noted in the literature where corrections have been applied[8] and where they are omitted.[9] The observed pseudo-first-order constants for the reaction of HOO^- and HO^- with 2,4-dinitrofluorobenzene (DNFB) and 2,4-dinitrochlorobenzene (DNClB) (see eq 4) afford linear plots of k_{obsd} vs. [B$_f$] and log k_{obsd} vs. pH, for the respective nu-

cleophiles. The rate constants, as well as rate ratios of this study, along with previous results[4,10] are given in Table III.

Table III. Second-Order Rate Constants for the Reaction of 1-Halo-2,4-dinitrobenzenes with Various Nucleophiles, $\mu = 1.0$, $t = 30°$. Rate Ratios for the Nucleophiles Are Provided in the Lower Column

Nucleophile	k_F	k_{Cl}	k_I
		M^{-1} min^{-1}	
Glycine[a]	19.0	0.015	2.2×10^{-2}
Hydrazine[a]	80.5	0.023	0.17
Glycylglycine[a]	4.4	7.0×10^{-3}	3.7×10^{-3}
Hydroperoxide anion	8.6×10^5	1.4×10^3	
Hydroxide	19	1.8×10^{-2}	
	Rate ratios		
Hydrazine/glycine	4.2	1.5	7.3
Glycine/glycylglycine	5.7	2.1	5.9
Hydrazine/glycylglycine	18.3	3.2	45
k_{HOO}-/glycine	4.5×10^4	9.6×10^4	
k_{HOO}-/k_{HO}-	4.5×10^4	7.8×10^4	

[a] See ref 4.

The loss in absorbance near 265 nm upon aminolysis or alcoholysis of methyl tosylate (5) affords a method of following this nucleophilic displacement reaction.
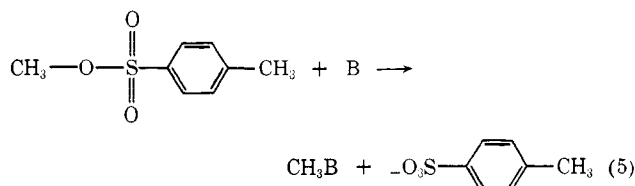
A plot of k_{obsd} vs. [B$_T$] (Figure 1) provided the pH-dependent second-order rate constant, which was multi-

(8) M. J. Gregory and T. C. Bruice, J. Amer. Chem. Soc., **89**, 4400 (1967).
(9) T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, ibid., **89**, 2106 (1967).
(10) J. F. Bunnett, ibid., **79**, 5969 (1957).

plied by the reciprocal of the mole fraction of free base present [i.e., $(K_a + a_H)/K_a$] to give the true second-order rate constants for aminolysis (k_3) and alcoholysis (k_4) (see Tables IV and V).

Table IV. Second-Order Rate Constants for the Aminolysis of Methyl Tosylate at $t = 30°$, $\mu = 1.0$ with KCl

Nucleophile	k_3, M^{-1} min^{-1}	No. k_{obsd}	Total buffer concn range	pK$_a$
Methoxylamine	3.9×10^{-2}	10	1.0–0.1	4.81
Trifluoroethylamine	9.5×10^{-2}	10	1.0–0.05	5.83
Glycylglycine	0.42	10	1.0–0.05	8.25
Hydrazine	0.39	10	1.0–0.1	8.11
Glycine	0.82	10	1.0–0.1	9.63

Table V. Second-Order Rate Constants for the Alcoholysis of Methyl Tosylate at $t = 30°$, $\mu = 1.0$ with KCl

Nucleophile	k_4, M^{-1} min^{-1}	No. k_{obsd}	Concn range	pK$_a$[a]
$CH_3CO_2^-$	3.0×10^{-3}	10	1.0–0.1	4.60
$CF_3CH_2O^-$	0.12	10	1.0–0.1	12.36
HOO^-	6.8	4	1.4×10^{-3}– 1.4×10^{-4}	11.6
$HC{\equiv}CCH_2O^-$	0.24	6	1.0–0.1	13.55
HO^-	0.15	11		15.74

[a] pK$_a$ values from T. C. Bruice, T. H. Fife, J. J. Bruno, and N. E. Brandon, Biochemistry, **1**, 7 (1962), at both 25 and 30°.

Discussion

The Brønsted plots obtained for the aminolysis or hydrazinolysis of 2,4-dinitrophenyl acetate are presented in Figure 2. One would anticipate that the nucleophilicity of a base exhibiting the α effect would be dependent upon its pK$_a$. Inspection of Figure 2 reveals that the substituted hydrazines fall on a line (eq 6, $\gamma = 0.998$) separate from that for primary amines (eq 7, $\gamma = 0.990$). By combining eq 6 and 7 a

$$\log k_{hydrazine} = 0.80 \text{ pK}_a - 2.31 \qquad (6)$$

$$\log k_{amines} = 0.57 \text{ pK}_a - 2.05 \qquad (7)$$

linear free energy expression for the α effect is obtained when 2,4-dinitrophenyl acetate serves as substrate (eq 8). Observations in this laboratory[4] indicate that plots

$$\alpha \text{ effect} = 0.23 \text{ pK}_a - 0.26 \qquad (8)$$

of log k_2 vs. pK$_a$ have parallel slopes for the addition of amines and hydrazines to malachite green. A similar observation has been noted for the addition of amines and hydrazines to carbon dioxide.[11]

From these limited results, one might inquire if parallel Brønsted plots are characteristic of one-step addition reactions. That different Brønsted slopes are obtained with 2,4-DNPA as substrate may reflect the kinetic importance of both bond-making and bond-breaking processes and, therefore, the nature of the leaving group. One would anticipate that as the α effector becomes a very poor nucleophile (i.e., semicarbazide) that bond-breaking processes will become more important and result in a gradual disappearance of the α effect. However, with a poorer nucleophile, bond-formation processes will also be greater in the transition state which

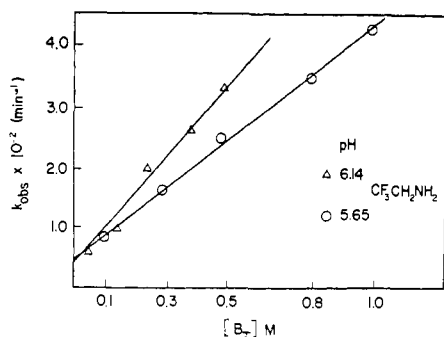(11) M. Caplow, ibid., **90**, 6795 (1968).

Figure 1. The linear dependence of the pseudo-first-order rate constants for the reaction of trifluoroethylamine with methyl tosylate at 2 pH values and 10 different concentrations.

Figure 2. Brønsted plot for the reaction of hydrazines, hydrazides, and methoxylamine with 2,4-dinitrophenyl acetate. The second-order rate constants for the reaction of amines with 2,4-DNPA are from reference 7.

should lead to an enhancement of the α effect, off-setting to some extent the importance of the leaving group. Thus, the combination of the two effects may result in Brønsted plots that are other than parallel. It should be emphasized that this explanation is by no means unequivocal and that it is based on, as yet, a limited number of reactions.

Rate constants for the reaction of nitrogen, oxygen, and carbon nucleophiles with malachite green are given in Table II. Although the nucleophiles are of widely different types, several generalizations may be made about their reactivities toward the stabilized "carbonium ion" of malachite green. The rate constants for reaction of H_2O and HO^- and CH_3O^- are generally smaller than the corresponding constants for primary amines of similar pK_a (see ref 4). Both ClO^- and HOO^-, having α electrons, are approximately three orders of magnitude more reactive than the oxyanions. Similar orders of nucleophilicity are obtained when activated esters are used as substrates.[9,12]

Equilibrium constants for additions to malachite green from this study (Table II) as well as those from previous studies (see ref 4 for pertinent references) indicate that α-effect nucleophiles' generally have more favorable equilibria than the corresponding nucleophiles not having α electrons when "hydrogen nucleophilicity" is used as the basis for comparison.[13] The larger equilibrium constants obtained for α-effect nucleophiles (NH_2NH_2, $RCONHNH_2$) may result from formation of a more stable product or from differences in the ground state of the starting materials. Ingold[14] has suggested that one of the adjacent nonbonding orbitals is in a high energy state resulting in destabilization of the ground state. Also, considerable evidence from nmr measurements on substituted hydrazines has been interpreted as reflecting unshared nonbonding electron pair repulsion.[15] The extremely low bond energies for the N–N bond in hydrazines and the O–O bond in substituted peroxides is reflected in adjacent nonbonding electron interactions.[16] However, the stabilities of oximes and hydrazines over the corresponding Schiff bases toward

hydrolysis may reflect unusual product stability of the former compounds. Thus, it may be that the contributions to a more favorable equilibria can be from either product stability or differences in the free energy of initial reactants and this may be influenced by the substrate employed.

In a comparison of kinetic and thermodynamic data, one notes that for HOO^- and ClO^- the decrease in $\Delta F^{\pm}$ far exceeds that for ΔF°. Thus, although the K_x values associated with HOO^- and HO^- are approximately equal, the rate constants for addition of these nucleophiles differ by approximately 10^4. Linear relationships have been obtained[13] when the logs of the second-order rate constants for reaction of alkoxide ions with p-nitrophenyl acetate (p-NPA) are plotted vs. the log of the equilibrium constant for addition of the same nucleophiles to several aldehydes. Since data for the anion of H_2O_2 do not deviate from this linear free energy correlation it must be concluded that factors affecting the rate of reaction with p-NPA also influence the equilibrium constant for addition of this species to aldehydes. A similar conclusion has been reached[4] for the neutral hydrazine species with malachite green as substrate since a plot of log k_1 vs. log K_x for primary amines and hydrazines is linear, the hydrazines exhibiting no positive deviation. Other nucleophiles, whose lower $\Delta F^{\pm}$ is not offset by a similar change in ΔF°, may include hydroxamic acids whose reactivity has been ascribed in some cases to be due to intramolecular base catalysis[17] and hypochlorite whose hyperreactivity may result from general (Lewis) acid catalysis by the chlorine atom.[18] Thus, from our observations it appears that α-effect nucleophiles may be divided into two groups: those that derive their unusual reactivities largely from thermodynamic properties ($MeONH_2$, NH_2NH_2) and those that do not (HOO^- and ClO^-).[19a,b]

(12) W. P. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.*, **82**, 1778 (1960).

(13) Also see E. G. Sanders and W. P. Jencks, *ibid.*, **90**, 6154 (1968), for a discussion on equilibrium constants for the reaction of aldehydes with α-effect and non-α-effect nucleophiles.

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969.

(15) M. J. S. Dewar and B. Jennings, *J. Amer. Chem. Soc.*, **91**, 3655 (1969).

(16) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); K. S. Pitzer, *J. Amer. Chem. Soc.*, **70**, 2140 (1948).
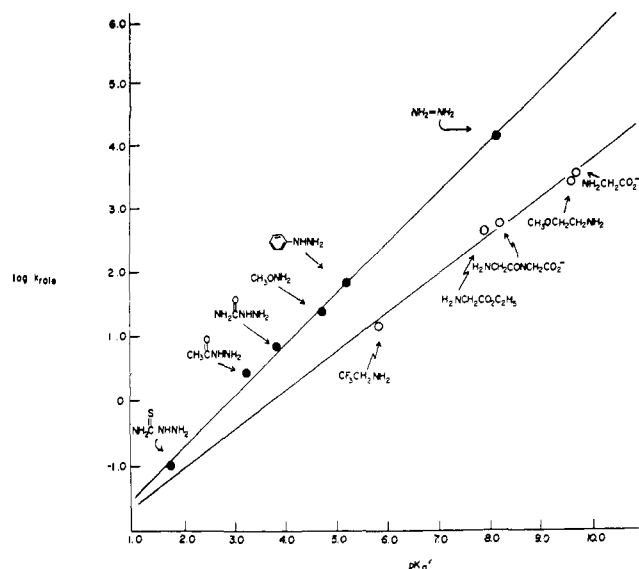
(17) J. D. Aubort and R. F. Hudson, *Chem. Commun.*, 938 (1970).

(18) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, San Francisco, Calif., 1969, p 108.

(19) (a) For a somewhat different classification of such compounds see J. D. Aubort and R. F. Hudson, *Chem. Commun.*, 937 (1970);

It should be pointed out that the division of α-effect nucleophiles into two groups is somewhat arbitrary because changes in $\Delta F°$ do have effects upon the reactivity of HOO^- and ClO^-; however, the greater reactivity of HOO^- and ClO^- is from sources other than a more favorable equilibria in the system studied.

The source of this unusual reactivity for HOO^- suggests from the high molar refraction that polarizability of hydrogen peroxide may result in some double bond character between the two oxygens.[18,20] Bunnett[10] has provided evidence (Table III) which indicates that, as the halogen substituent on 2,4-dinitrohalobenzenes becomes more polarizable, the attack of a polarizable nucleophile (thiophenoxide) has an enhanced rate over that of less polarizable nucleophiles (piperidine or methoxide). Therefore, if polarizability is one of the factors responsible for the unusual reactivity of HOO^- it was anticipated that it would show an enhanced rate (over nonpolarizable nucleophiles) when more polarizable substrates were employed. The results of this study are shown in Table III. The differences in the rate ratios for amine:hydrazine have been interpreted[4] as reflecting varying importances of the attack and departure steps (i.e., changes in the position of the transition state along the reaction coordinate) when the leaving group is changed from F to Cl. The fact that the rate ratio for HOO^-/glycine increases by a factor of 2.1 when going from DNFB to DNClB, while the usual trend when comparing an α effector with a nonpolarizable nucleophile results in a ratio less than one, may reflect the importance of polarizability. The change in rate ratio is by no means comparable to that of 33 for $C_6H_5S^-$/CH_3O^-. These findings are by no means incompatible with polarizability of HOO^- and they serve in some degree to indicate that it may be at least partially responsible for its unusual reactivity.

A clear manifestation of the difference in importance of a more favorable equilibria to the α effect exhibited by hydrazines on the one hand and HOO^- on the other is the difference in sensitivity of the α effect to the Brønsted β constant for nucleophilic reactivity. It is generally accepted that the magnitude of the Brønsted β may be correlated with the relative position of the transition state along the reaction coordinate (although this correlation is by no means unequivocal; see ref 4, 21). There seems to be a good correlation between the magnitude of β and the magnitude of the α effect for hydrazine. This does not appear to be so with HOO^-. Table VI provides both HOO^-/$CF_3CH_2O^-$ and HOO^-/HO^- rate ratios. Because both HO^- and $CF_3CH_2O^-$ are stronger bases (i.e., $pK_a = 15.74$ and 12.36, respectively) than HOO^- ($pK_a = 11.6$) the rate ratio should be smaller than unity if the α effect disappears. Although values of β are generally not available for the reaction with oxyanions, so one cannot compare the magnitude of β with the magnitude of the α effect, two comparisons serve to demonstrate that the values of β are usually smaller, but not drastically different in size from

(b) G. M. Blackburn and W. P. Jencks, J. Amer. Chem. Soc., 90, 2638 (1968). The reaction of methyl formate with hydrazine appears to represent a case where hydrazine does not derive its reactivity from thermodynamic properties.
(20) (a) J. W. Bruhl, Ber., 28, 2847 (1895); (b) P. A. Giguere, Can. J. Res., Sect. B, 21, 156 (1943); (c) P. A. Giguere and P. Geoffiron, ibid., Sect. B, 27, 168 (1949).
(21) (a) R. A. Marcus, J. Amer. Chem. Soc., 91, 7224 (1969); (b) R. A. Marcus, J. Phys. Chem., 72, 891 (1968).

Table VI. Rate Ratios for the Reaction of Various Substrates with HOO^-/$CF_3CH_2O^-$ and HOO^-/HO^-

Substrate	HOO^-/$CF_3CH_2O^-$	$\beta_{RO^-}{}^a$
$CH_3C(=O)-O-C_6H_5$ [b]	80	0.66
$CH_3C(=O)-O-C_6H_4-NO_2$ [c]	58	
$CH_3C(=O)-O-C_6H_3(NO_2)_2$ [c]	41	
$CH_3C(=O)-O-N^+C_5H_5$ [c]	51	
$CH_3-O-S(=O)_2-C_6H_4-CH_3$	62	0.20
	HOO^-/HO^-	
$Si(O-C(=O)-CH_2C(=O)-CH_3)_3$ [d]	50	
$C_6H_5CH_2Br$ [d]	35	
[(CH_3)_2N-C_6H_4]_2C^+-C_6H_5 ... N(CH_3)_2	10^4	

[a] β values are provided when they are known, and where there is a linear relationship between log k and pK_a over the range of pK_a studied. [b] T. C. Bruice, T. H. Fife, J. J. Bruno, and N. E. Brandon, Biochemistry, 1, 7 (1962). [c] Reference 7. [d] R. G. Pearson and D. N. Edgington, J. Amer. Chem. Soc., 84, 4607 (1962).

those of amines. Both p-nitrophenyl acetate and methyl tosylate exhibit β values for amines of 0.83 and 0.25, respectively, while the corresponding values for oxyanions are 0.66 and 0.20. It should also be noted that in a number of cases plots of log k against pK_a of alkoxide ion are nonlinear, so that β decreases as the pK_a of the nucleophile increases. Thus, in these systems β changes over a reasonably narrow range of pK_a. Inspection of Table VI reveals that the ratio of rates never falls below 35. Thus, it would seem that factors present in the reaction of HOO^- are less prevalent or absent with NH_2NH_2.[7] Therefore, although both compounds are α effectors, HOO^- seems to derive some of its "hyperreactivity" from sources other than thermodynamic properties, although the latter effect is present to some degree.

The data of this study on the nucleophilic displacement reactions on methyl tosylate probably deserve special comment since the electrophilic center is sp^3 hybridized. Considerable verbiage has been expended on the question of whether the kinetic α effect is observable when attack involves the sp^3-hybridized carbon.[9,12] The Brønsted plot for amine nucleophiles reacting with
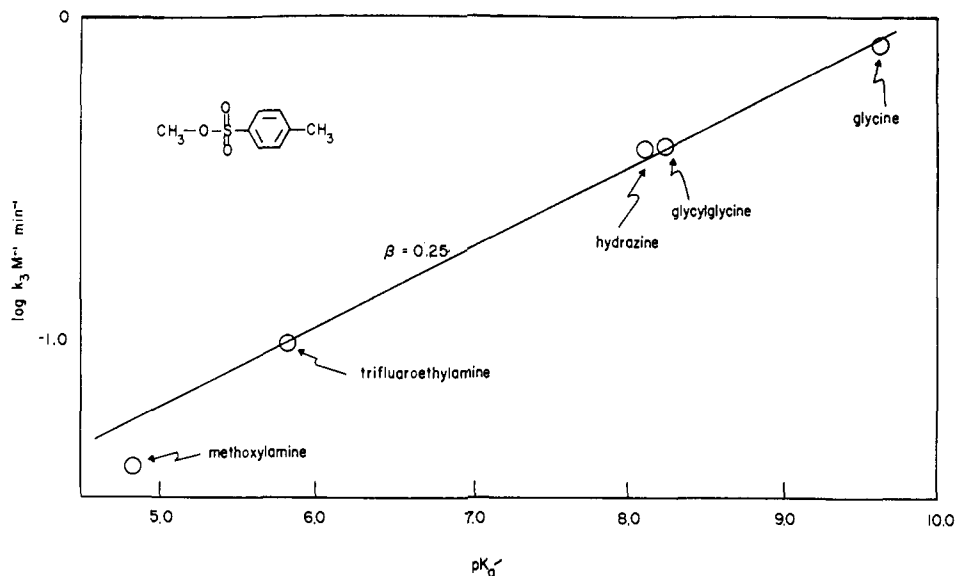
Figure 3. Brønsted plot for the reaction of primary amines, hydrazine, and methoxylamine with methyl tosylate.

methyl tosylate is presented in Figure 3. Inspection of Figure 3 reveals that amine, hydrazines, and methoxylamine fall on a single line whose slope is 0.27 (eq 9), the correlation coefficient being 0.995. It should also

$$\log k_{\text{rate}} = 0.27 \, pK_a - 2.7 \tag{9}$$

be noted that the aminolysis and hydrazinolysis of methyl iodide (β = 0.22) do not exhibit the α effect.[8] In sharp contrast to the reaction of amines and hydrazines with methyl tosylate, peroxide anion exhibits a large positive (Table V) deviation from the Brønsted plot for oxyanions (eq 10) even though β

$$\log k_{\text{rate}} = 0.20 \, pK_a - 2.4 \tag{10}$$

is again extremely small (Figure 4). It would thus appear as though the α effect is manifested in HOO⁻ attack on sp³ carbon.[22] Wiberg[23] has suggested that differences in solvation of HOO⁻ as compared to HO⁻ may account for the hyperreactivity of HOO⁻ toward

(22) Also see A. R. Fersht and W. P. Jencks, *J. Amer. Chem. Soc.*, **92**, 5442 (1970), where β is again small and HOO⁻ is unusually reactive toward sp² carbon.
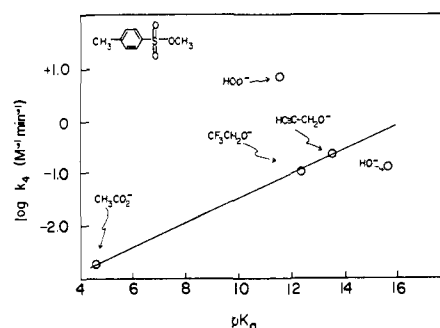(23) K. B. Wiberg, *ibid.*, 77, 2519 (1955).

Figure 4. Brønsted plot for the reaction of methyl tosylate with peroxide anion and other oxyanions.

benzonitrile. However, solvation of HO⁻ makes it a poorer nucleophile than alkoxide ions of similar basicity which are still poorer nucleophiles than HOO⁻.[9] Thus, the effect of solvation cannot explain completely the positive deviation of HOO⁻ from other oxyanions.