The properties of **3a**,**d**–**f** correspond to those reported (see Table V for references).

2-Methyl-3-*p*-anisyloxaziridine (**3b**): mass spectrum, (70 eV), *m/e* (relative intensity) 165 (M^+, 60), 136 (25), 135 (100), 107 (43), 78 (68); NMR δ 2.30 (s, 0.87 H), 2.73 (s, 2.13 H), 3.70 (s, 2.13 H), 3.75 (s, 0.87 H), 4.15 (s, 0.71 H), 4.90 (s, 0.29 H), 6.9 (m, 4 H); active oxygen calcd for $C_9H_{11}NO_2$ 9.7%, found 9.4% (corrected for purity).

2-Methyl-3-*p*-chlorooxaziridine (**3c**): mass spectrum, (70 eV), *m/e* (relative intensity) 169 (M^+, 60), 168 (63), 141 (33), 139 (100), 110 (10); NMR δ 2.35 (s, 1.08 H), 2.82 (s, 1.92 H), 4.28 (s, 0.64 H), 5.03 (s, 0.36 H), 7.30 (s, 2.56 H), 7.37 (s, 1.44 H); active oxygen calcd for $C_8H_{10}NOCl$ 9.4%, found 9.4% (corrected for purity).

Amides were prepared by reaction of benzyl chlorides with NH_3 or alkylamines in the presence of NaOH. Melting points corresponded to those reported as follows: **4a**,[19] **4b**,[22] **4c**,[23] **4d**,[20] *p*-anisamide,[21] and *p*-chlorobenzamide.[21] N-*tert*-Butyl-*p*-anisamide: mp 140–141.5 °C; mass spectrum, *m/e* 207 (M^+). N-*tert*-Butyl-*p*-chlorobenzamide: mass spectrum, *m/e* 213 (M^+).

N-Arylformamides were prepared by condensation of anilines with ethyl formate. Melting or boiling ranges corresponded to those reported in the following: *N*-methylformanilide,[24] *p*-anisylformamide,[2b,25] p-chlorophenylformamide.[26]

N-Methyl-*N*-*p*-anisylformamde (**5b**): UV (MeOH) λ_{max} 237 nm (log ϵ 3.96); bp 160–171 °C (4 mm); mass spectrum, *m/e* (relative intensity) 165 (M^+, (30), 136 (9), 125 (8), 124 (100), 122 (56), 108 (9), 96 (3), 94 (3), 43 (22).

Photolyses. Solutions of oximes or oxaziridines ($\sim 10^{-2}$ M) in ethanol were irradiated with UV light from a 300-W high-pressure Hg lamp (Halos HIP 300). Photolyses of oximes were followed by monitoring the disappearance of starting material by TLC, and product analyses were carried out by GLC. Photolyses of oxaziridines were performed under nitrogen with irradiation through a quartz filter. The progress of the reaction was monitored by iodometric determination of active oxygen, and reaction products were analyzed by GLC and GC/MS.

Quantum Yields. Quantum yields in photolyses were measured by irradiating 35 mL of ethanol solutions of substrates ($\sim 2 \times 10^{-2}$ M) in 40-mL quartz tubes in a merry-go-round apparatus equipped with a 60-W low-pressure Hg lamp that emitted 254-nm light. Light intensities were measured with a potassium ferrioxalate actinometer.[27] The amount of light quanta absorbed was 3.58×10^{-6} einstein/min. Disappearance of substrate was followed by HPLC for oximes and by iodometry for oxaziridines. The HPLC analyses were performed on a JASCO high-performance liquid chromatograph (Twincle) equipped with a Finepack Sil NH_2 column eluted with dioxane at a flow rate of 1 mL/min. A UV detector at 250 nm was used. The *E* aldoximes (trans) have retention times t_R of 3.6, 3.7, and 3.5 min for **2a**, **2b**, and **2c**, respectively.

Registry No. (*E*)-**2a**, 622-31-1; (*Z*)-**2a**, 622-32-2; (*E*)-**2b**, 3717-21-3; (*Z*)-**2b**, 3717-22-4; (*E*)-**2c**, 3717-24-6; (*Z*)-**2c**, 3717-23-5; *cis*-**3a**, 39245-63-1; *trans*-**3a**, 40264-03-7; *cis*-**3b**, 82044-36-8; *trans*-**3b**, 82044-37-9; *cis*-**3c**, 82044-38-0; *trans*-**3c**, 82044-39-1; *trans*-**3d**, 3585-81-7; *trans*-**3e**, 82079-47-8; *trans*-**3f**, 82044-40-4; 2-methyl-3-[*p*-(dimethylamino)phenyl]oxaziridine, 82044-41-5; 2-*tert*-butyl-3-[*p*-(dimethylamino)phenyl]oxaziridine, 82044-42-6; benzophenone oxime, 574-66-3; *p*-methoxybenzophenone oxime, 54150-63-9; fluorenone oxime, 2157-52-0.

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Nucleophilic Catalysis of the Hydrolysis of Phenyl Acetates by the Succinimide Anion in Aqueous Solution

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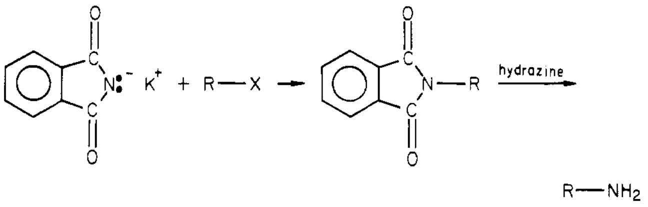
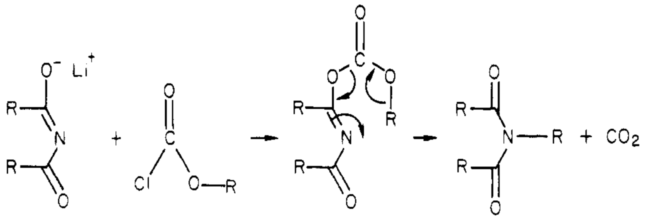
Kinetic studies were conducted on the disappearance of some phenyl acetates in aqueous solutions buffered by succinimide/succinimide anion at 30 °C. The most reasonable mechanistic scheme, compatible with the data, is that shown in Scheme I involving nucleophilic displacement by the succinimide anion on the ester. The rate equation (eq 2) may be derived from the mechanism of Scheme I. The values of pseudo-first-order rate constants which were determined may be predicted by eq 2 and the constants of Table I with an error of 7% or less (see Table II). Phenyl acetate was the only substrate that had no buffer-dependent disappearance. Although succinimide is converted to succinamic acid by hydrolysis in the buffered solutions used, only about 6% or less of succinimide is lost during the time required for substrate disappearance. The nucleophilic role for the succinimide anion was assigned on the basis of a high Hammett ρ value (2.25) for the three phenyl acetates studied and the low solvent deuterium isotope rate effect of 1.13 obtained for the *p*-nitrophenyl acetate substrate. The low value for the nucleophilic rate constant obtained by *p*-nitrophenyl acetate cannot be ascribed to ground-state charge delocalization as estimated by MINDO-3 calculations utilizing frontier molecular orbital theory. This observed low reactivity is therefore thought to be the result of a tight anionic solvation shell in the aqueous solutions employed. Media studies in different salts on this reaction show little effects. Finally, the absence of third-order rate terms involving succinimide in this reaction is due to the inability of the succinimide anion to have its nucleophilicity increased by proton removal in the transition state.

The nucleophilicity of imide anions is well-documented by the Gabriel synthesis of primary amines, involving the S_N2 displacement of halogen atoms from primary alkyl halides.[1]

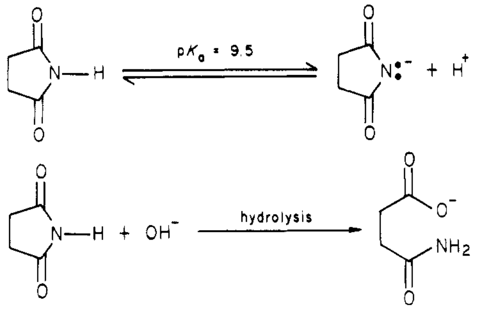


Acyl-displacement reactions have also been observed with these anions. The reaction of the lithium anion of a number of imides with alkyl chloroformates is accompanied by loss of carbon dioxide, affording the corresponding *N*-alkyl imide.[2] The mechanism proposed involves the decomposition of the initially formed O-acylated imide as shown.



Scisson of a benzoyl group has been reported during reaction of 2-bromo-1,3-diphenyl-1,3-propandione with potassium phthalimide in ethanol.[3]

Succinimide, a partially water-soluble weak acid (pK_a = 9.5),[4] can be titrated accurately in nonaqueous media.[5] It hydrolyzes very slowly in aqueous alkaline solutions, affording succinamic acid as the initial product by attack of the hydroxide ion on its acid form.[4] The hydrolysis reaction is thus retarded at pH's above the pK_a. The above properties, in addition to the large ground-state resonance stabilization possible, have lead to a decision to study the kinetics of the reaction of phenyl acetates with the succinimide anion in aqueous solution.



The rate of production of *p*-nitrophenolate anion in aqueous solutions of *p*-nitrophenyl acetate (PNPA) buffered by succinimide (SH)/succinimide anion (S^-) was measured using a visible–UV spectrophotometer thermostated at 30 ± 0.3 °C. Reactions in five serial dilutions ranging from 0.1 to 1.0 M total buffer concentration were conducted at each of six different pH's ranging from 8.5 to 10.3. Potassium chloride was added to each in order to maintain a constant ionic strength value of 1. In all cases, buffer concentrations were at least 100 times greater than that of the substrate. Under these conditions, all data correlate well with the first-order kinetic equation (eq 1)

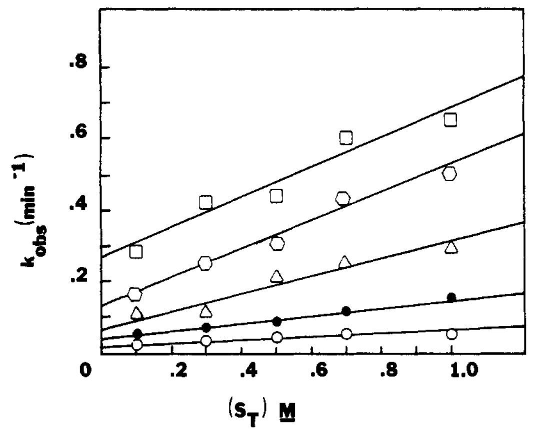


Figure 1. Plots of the pseudo-first-order rate constants for the reaction of PNPA vs. the molar concentrations of S_T in Water at 30 °C: (○) pH 8.51, (●) pH 8.89, (△) pH 9.45,(○)pH 9.90, (□) pH 10.25.

Table I. Values for Rate Constants Obtained by a Fit of the Kinetic Data for Phenyl Acetates to Equations 2 or 5 at 30 °C and μ = 1.0

ester	k_n, L mol^{-1} min^{-1}	k_{hyd}, L mol^{-1} min^{-1}	k'_{H_2O}, min^{-1}
PNPA(H_2O)	0.51 ± 0.02	970 ± 118	0.008
MNPA(H_2O)	0.140 ± 0.01	705 ± 85	
PCPA(H_2O)	0.0073 ± 0.001	464 ± 50	
PA(H_2O)		212 ± 20	

$$\frac{-d[\text{ester}]}{dt} = k_{obsd}[\text{ester}] \qquad (1)$$

to better than 3 half-lives. The 30 pseudo-first-order rate constants (k_{obsd}) obtained are correlated by the rate expression of eq 2. Plots of k_{obsd} values vs. the total suc-

$$k_{obsd} = k_n\left[\frac{K_a'}{K_a' + a_n}\right][S_T] + k_{hyd}[OH^-] + k_{H_2O}' \qquad (2)$$

cinimide concentration ($S_T = S^- + SH$) afford straight lines for dilutions at each pH (see Figure 1). The k_n value obtained is the average of six values from the slope of the plots at each pH according to eq 3. The value of the K_a'

$$k_n = \text{slope}/[K_a'/(K_a' + a_h)] \qquad (3)$$

determined was 9.51 (see Experimental Section) and a_h is the activity of the hydrogen ion from glass electrode measurements. The k_{hyd} value from eq 2 is obtained as the slope of a plot of the intercepts of the k_{obsd} vs. [S_T] plots vs. the hydroxide ion concentration at each pH according to eq 4. The very slight water rate obtained, k_{H_2O}' for PNPA only is the intercept of this latter plot.

$$\text{intercept} = k_{hyd}[OH^-] + k_{H_2O}' \qquad (4)$$

In order to determine solvent deuterium isotope rate effects on this reaction, a few experiments were conducted in deuterium oxide solvent. Three SH/S^- buffer dilutions at pD 9.95 were prepared ranging from 0.1 to 1.0 M total buffer, and the rate of production of the *p*-nitrophenolate anion was measured in these solutions. Potassium chloride was used to maintain a constant ionic strength of 1. Kinetic studies were conducted as in water. Values for k_n and k_{hyd} were obtained as before from a three-point plot of k_{obsd} vs. [S_T].

The reaction of SH/S^- buffers with *p*-chlorophenyl acetate (PCPA), *m*-nitrophenyl acetate (MNPA), and

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(1) M. S. Gibson and R. W. Bradshaw, *Angew. Chem., Int. Ed. Engl.*, 7, 919 (1968).

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(4) J. T. Edwards and K. A. Terry, *J. Chem. Soc.*, 3527 (1957); M. N. Khan and A. A. Khan, *J. Org. Chem.*, **40**, 1793 (1975).

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Table II. Comparison of Experimentally Determined and Calculated Pseudo-First-Order Rate Constants for PNPA at pH 9.50

[buffer],[a] M	k_{obsd} (det), min^{-1}	k_{obsd}(calcd), min^{-1}
0.1	0.079	0.071
0.3	0.103	0.123
0.5	0.192	0.173
0.7	0.219	0.224
1.0	0.289	0.300

[a] Molar concentration of total buffer. [b] Calculated with the aid of eq 2 and the values for the rate constants appearing in Table I for PNPA.

Table III. Media Studies on the Rate Constants for PNPA at pH 9.50 (30 ± 0.3 °C)

solvent	added salt[a]	k_n,[b] L mol^{-1} min^{-1}	k_{hyd},[b] L mol^{-1} min^{-1}
H_2O	none	0.473 ± 0.02	1097 ± 118
H_2O	KCl	0.482 ± 0.02	1080 ± 118
H_2O	LiCl	0.473 ± 0.02	2580 ± 300
H_2O	$(CH_3)_4NCl$	0.440 ± 0.02	2650 ± 300
D_2O	KCl	0.418 ± 0.02	2000 ± 300

[a] Used to maintain ionic strength at a constant value of 1.0. [b] Determined with the aid of eq 2.

phenyl acetate (PA) was also studied at pH's 8.95, 9.50, and 10.05. Reactions in five serial dilutions ranging from 0.1 to 1.0 M buffer were prepared for each ester at each pH value. Again, potassium chloride was used to maintain a constant ionic strength of 1. Kinetic studies were conducted as with PNPA in water. These data also correlate well with eq 1, and the k_{obsd} values obtained correlate with eq 2, except for those k_{obsd} values from phenyl acetate. The rate of disappearance of phenyl acetate was buffer independent, and thus eq 5 was used instead of eq 2 to correlate

$$k_{obsd} = k_{hyd}[OH^-] \qquad (5)$$

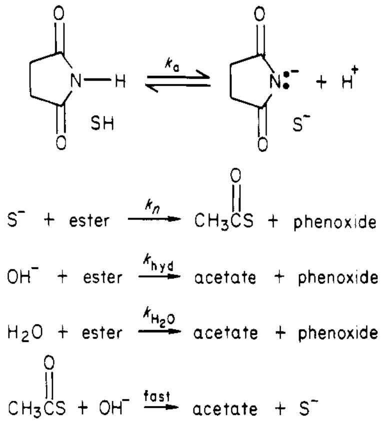
those k_{obsd} values. All k_n and k_{hyd} values obtained are listed in Table I. The rate constants shown in Table I are capable of predicting k_{obsd} values using eq 2 to an accuracy of 7%. Representative calculated k_{obsd} values for PNPA are compared to experimental values for pH 9.50 in Table II. Values of k_{hyd} and k_{H_2O}' for all esters obtained agree with such numbers determined previously. Bruice and Lapinski[6] obtained a value for k_{hyd} of 990 L mol^{-1} min^{-1} and a value for k_{H_2O}' of 8.6×10^{-5} L mol^{-1} min^{-1} for PNPA. Bruice and Mayahi obtained k_{hyd} values of 638, 417, and 223 L mol^{-1} min^{-1}, respectively, for MNPA, PCPA, and PA.[7]

Table III shows the values obtained for k_n and k_{hyd} from the D_2O experiments and a salt study of the reaction of PNPA. All entries from experiments conducted in water in the table come from a series of three buffer dilutions at pH 9.50 using the added salt shown (column 2) to maintain constant ionic strength. Rate constants were determined and calculated as already stated.

Table IV. Comparison of Pseudo-First-Order Rate Constants Determined for the Hydrolysis of Succinimide at 30 °C in Aqueous Carbonate Buffer to Those Calculated with the Aid of Equation 7

[buffer], M	pH	k_e(det), min^{-1}	k_e (calcd), min^{-1}
0.01	10.12	0.00283	0.00458
0.05	10.46	0.00333	0.00533
0.10	10.60	0.00398	0.00551

Scheme I



Edwards and Terry have shown that succinimide slowly hydrolyzes to succinamic acid in aqueous alkaline solutions according to the rate law of eq 6.[4] The pseudo-first-order

$$\frac{-d[S_T]}{dt} = k_e[S_T] \qquad (6)$$

rate constants (k_e) are given by eq 7, where k_2 is the second-order rate constant for the reaction of succinimide with the hydroxide ion and α is the fraction of imide ionized [i.e. $\alpha = K_a'/(K_a' + a_H)$].

$$k_e = \frac{k_2 K_w \alpha}{K_a'} \qquad (7)$$

Since significant loss of buffer to hydrolysis would mean error in the values of rate constants obtained for the ester hydrolysis reaction, it is desirable to be certain of the hydrolysis rate of the succinimide itself. Accordingly, three serial dilutions of aqueous carbonate buffer were prepared at pH 10.5. The disappearance of succinimide in each buffer was measured spectrophotometrically at 30 °C. The k_e values obtained using eq 6 are shown in column 3 of Table IV.

The k_e values listed in column 4 of Table IV were calculated with the aid of eq 7 using the value of 128 ± 9 L mol^{-1} min^{-1} obtained for k_2 by Edwards and Terry. The value of K_a' was the same as that obtained in the present study (see Experimental Section). Agreement between experimentally determined and calculated values for k_e seems satisfactory, taking into account the 5 °C temperature difference between the two studies, for the purposes of the discussion which follows.

Discussion

The hydrolysis of succinimide is too slow to interfere with the reaction of S^- with the phenyl acetates. To show this, integration of eq 6, followed by removal of logarithms, affords eq 8. The change in the term $e^{-k_e t}$ at any pH

$$[S_T]_t = [S_T]_0 e^{-k_e t} \qquad (8)$$

affords a look at the loss of S_T with time. At time zero, the term $e^{-k_e t} = 1$; therefore, the difference between its value at time t and time zero affords the percent of succinimide lost. Indications are that no more than 6–8% of the buffer is lost to hydrolysis during the time that it takes to conduct the kinetic studies on any of the phenyl acetates in this study. Therefore, the k_n values calculated in Tables I and III are correct.

The mechanism of Scheme I affords eq 2 as its rate law and is favored as being correct for the reaction. Initially, succinimide loses a proton, affording the anionic nucleophilic species, S^-. Attack of the anion on the ester produces a tetrahedral intermediate which can decompose into

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[6] T. C. Bruice and R. Lapinski, *J. Am. Chem. Soc.*, **80**, 2265 (1958).
[7] T. C. Bruice and M. F. Mayahi, *J. Am. Chem. Soc.*, **82**, 3067 (1960).

N-acetylsuccinimide and the appropriate phenoxide. Concurrently, *N*-acetylsuccinimide is rapidly transformed to acetate and succinimide by reaction with the hydroxide ion and water. The lability of *N*-acetylsuccinimide to the hydroxide ion is already known.[8]

Plots of the observed data thus afford the rate constant for unassisted nucleophilic attack of S^- on the ester. Kinetically equivalent mechanisms in which succinimide or its anion have assistance roles are not favored on the strength of two factors. A Hammett plot (i.e., $\log k$ vs. σ) for the three phenyl acetates studied affords a straight line with a slope (i.e., ρ) of 2.25 in accord with previously determined values for second-order reactions involving amines or oxyanions and phenyl acetates.[9] ρ values determined for third-order rates involving phenyl acetates are usually one-fourth these quantities.[9] In preparing the plot, it was necessary to use $\sigma = 1.00$ (a value used previously for nucleophilic reactions of phenyl acetates) for the *p*-nitro group rather than 1.27.[10] The second factor involves the very slight deuterium isotope rate effect of 1.13 observed for PNPA (see Table III). Deuterium rate effects on second-order terms are usually of this magnitude for the aminolysis of phenyl acetates, while those observed for third-order terms are usually in the neighborhood of 2.0.[9]

The value for k_n of 0.51 L mol^{-1} min^{-1} obtained for PNPA (see Table I) can be compared to that for other nitrogen and oxygen nucleophiles. Placing the succinimide anion rate constant on a Bronsted plot obtained from second-order rate constants for some 40 amine and oxyanion nucleophiles[11] indicates that, although it is in the lower edge of the bandlike plot at a pK_a' of 9.5, it is some 80 times less nucleophilic than normal amine molecules toward PNPA. The explanation does not appear to be available from frontier orbital theory.[12] MINDO-3 calculations[13] on ammonia and the succinimide anion gave the following data.

nucleophile		charge on nucleophilic atom	HOMO energy, eV
S^-	N	−0.55	−3.4
	O	−0.67	
NH_3		−0.17	−10.1

The energy of the LUMO of PNPA may be estimated to be about 1 eV.[12] The energy of the HOMO of S^- is higher than that for ammonia; therefore, on the basis of the greater HOMO–LUMO overlap, the S^- should be most reactive. The S^- should also be most reactive on the basis of charge considerations, since either oxygen or nitrogen have three times the charge present on the ammonia nitrogen atom.

The explanation for the low nucleophilicity of S^- compared to ammonia must then lie in solvation differences by the water solvent. This seems reasonable, since the presence of the greater negative charge on the nitrogen or oxygen atoms of the anion should result in a tighter hydration shell than would be expected about the nitrogen atom of the ammonia molecule. The nucleophilicity of the anion is hampered by the extra energy needed to clear away the tight solvation shell. This would not be a problem for the basicity of the anion because protons can pass directly through the shell. The small effect on k_n observed in the media studies on PNPA (see Table III) may be interpreted to refute this explanation, since the strength of forces involved in solvation shells would be expected to be related to the ionic strength of the medium. However, all media employed in this study are polar and thus may not produce an observable change in solvation.

The inverse deuterium rate effect observed of 0.55 (i.e., k^{H_2O}/k^{D_2O}) for the k_{hyd} term for PNPA (see Table III) reflects the differences in basicity of these two lyate bases ($pK_a'^{D_2O} - pK_a'^{H_2O} = 0.4$).[14] The significant salt effect observed for this term with lithium and tetramethylammonium cations (see Table III) may be due to activity changes of the hydroxide ion, since pH measurements are also significantly affected in the presence of these ions.

Ester aminolysis may involve third-order rate paths which are usually explained as self-assisted nucleophilic attack (i.e., either general-acid or general-base catalysis by the amine).[9] Although one would perhaps not expect that such terms would be needed in this instance for the good *p*-nitrophenoxide leaving group,[7] it is at first surprising that none exists for phenyl acetate and the less reactive esters.[15] It is, however, not easy to visualize a viable mechanistic path utilizing self-assisted attack by the succinimide anion in ester imidolysis. Assistance by succinimide itself is possible, but general-acid catalysis of ester aminolysis usually occurs for only the least basic amines (i.e. pK_a's of the order of 5–6).[9,15]

Thus, it remains for the charged and tightly solvated succinimide anion to compete in entirely second-order processes with the powerful hydroxide ion for the ester molecule. This it does reasonably well when good leaving groups are present but not at all well for less reactive esters such as phenyl acetate. It is possible to estimate what the k_n term should be for S^- and phenyl acetate if it can be assumed that because NH_4^+ and SH have about the same acidity (pK_a' = 9.3 and 9.5, respectively):

$$\left(\frac{k_n^{PA}}{k_n^{PNPA}}\right)_{NH_3} \approx \left(\frac{k_n^{PA}}{k_n^{PNPA}}\right)_{S^-} \tag{9}$$

Since:

$$\left(\frac{k_n^{PA}}{k_n^{PNPA}}\right)_{NH_3} = \frac{0.245}{29.2} = 8.4 \times 10^{-4}{}^{7} \tag{10}$$

$$(k_n^{PA})_{S^-} = 8.4 \times 10^{-4}\,(k_n^{PNPA})_{S^-} = 0.0043 \tag{11}$$

Assuming $(k_n^{PA})_{S^-}$ is about 4.3×10^{-3} L mol^{-1} min^{-1} at a pH of 9.5, the rate of S^- nucleophilic attack on phenyl acetate would be barely detectable under the experimental conditions.

Experimental Section

Materials. Eastman red and white label succinimide was recrystallized from alcohol (95%) and dried in air, mp 124–125 °C. *p*-Nitrophenyl acetate was prepared from equal quantities of acetic anhydride and *p*-nitrophenol in pyridine. After heating a few hours on the steam bath, the reaction mixture was poured into ice–water and the solid precipitate was filtered off by suction. The precipitate was recrystallized to a white solid (mp 77–79 °C) from alcohol–water mixtures. The other phenyl acetates (*m*-NO_2, mp 53.8–54.2 °C; *p*-chloro, bp 91 °C, n^{21}_D 1.5172; unsubstituted, n_D 1.5018) were samples prepared for another study.[7] Deuterium

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[8] H. Boyd, I. C. Calder, S. J. Leach, and B. Milligan, *Int. J. Peptide Protein Res.*, **4**, 109 (1972).

[9] T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *J. Am. Chem. Soc.*, **89**, 2106 (1967).

[10] T. C. Bruice and S. J. Benkovic, *J. Am. Chem. Soc.*, **86**, 418 (1964).

[11] W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

[12] G. Klopman, "Chemical Reactivity and Reactions Paths", Wiley-Interscience, New York, 1974, Chapter 5.

[13] M. L. Olson and J. F. Chiang, *QCPE*, **11**, 309 (1976).

[14] T. H. Fife and T. C. Bruice, *J. Phys. Chem.*, **65**, 1079 (1961).

[15] W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 675 (1960).

oxide, 99.7%, was supplied by the Atomic Energy Commission. Potassium chloride and lithium chloride were Eastman red and white label. All salts were used as supplied.

Apparatus. Spectrophotometric kinetic measurements were conducted on a Beckman Model 5270 spectrophotometer equipped with an Acta M series autosampler. The sample cell was thermostated by circulated water at 30 ± 0.3 °C using a Precision Scientific Model 154 low temp temperature regulator. Measurements of the pH of the buffer solutions were conducted inside the temperature bath with a Sargent-Welch Model 830076 combination electrode. For reactions conducted in deuterium oxide, the pD was determined by adding 0.37 to the reading obtained for the glass electrode.[14]

Kinetic Procedure. Aqueous solutions buffered by succinimide/succinimide anion were prepared no more than 15 min before use by the addition of calculated amounts of standard aqueous potassium hydroxide to aqueous solutions of known concentrations of succinimide. The ionic strength of each buffer was maintained at 1 (unless otherwise stated) by addition of potassium chloride (except where lithium or tetramethylammonium chloride were used). Dilute dioxane solutions of the phenyl acetates were prepared and stored at 0 °C. A reaction was initiated in each buffer solution by addition of about 0.01 mL of the appropriate dioxane solution to 2.5 mL of the buffer in a cuvette. The cuvette containing the buffer had been previously thermostated in the cell holder of the spectrophotometer and, after momentary shaking, was returned to that position where absorbance due to the appropriate phenolate anion was measured by the instrument over an appropriate time period. The following wavelengths were employed: *p*-NO_2, 400 nm; *m*-NO_2, 350 nm; *p*-Cl, 285 nm; unsubstituted, 275 nm. The total succinimide concentration in the buffered solutions ranged from 0.1 to 1.0 M, while the concentration of phenyl acetate was always about 10^{-5} M. The pH of each buffer was recorded before and after each kinetic run. Each buffer was prepared to a pH tolerance of about 0.10 pH unit, while the pH drifted, on the average, 0.03 pH unit during the reaction. The values of K_w in water and in deuterium oxide at 30 °C that were employed were 1.48×10^{-14} and 2.24×10^{-15}, respectively. The pK_a values employed for succinimide in water and deuterium oxide were determined to be 9.51 and 9.95, respectively, at 1 M buffer by the method of half-neutralization. They agree with the value of 9.50 determined spectrophotometrically in water by Edwards and Terry.[4] Dilution of the buffer to 0.1 M solution resulted in a drift to lower pK_a' values of about 0.1 pH unit. Water used was doubly distilled from a glass apparatus.

A few experiments were conducted on the hydrolysis of succinimide itself similar to those of Edwards and Terry.[4] Aqueous 0.1 M potassium carbonate buffer solutions were prepared by dissolving calculated amounts of potassium carbonate and potassium bicarbonate in water. Three dilutions of this buffer were prepared containing 5×10^{-3} M succinimide. The rate of disappearance of succinimide was then measured spectrophotometrically at 235 nm at 30 ± 0.3 °C.

Pseudo-first-order rate constants were calculated using eq 12

$$k = \frac{\ln (\mathrm{OD}_\infty - \mathrm{OD}_0)/(\mathrm{OD}_\infty - \mathrm{OD}_t)}{t} \qquad (12)$$

with the aid of a weighted least-squares program written for an Oliveti-Underwood programmable 100 desk computer. Representative numbers of these computations were plotted to ensure that the reactions were indeed conducted under first-order conditions.

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Reactions of *N*,*N*-Dimethylvinylamine with Electron-Poor Olefins

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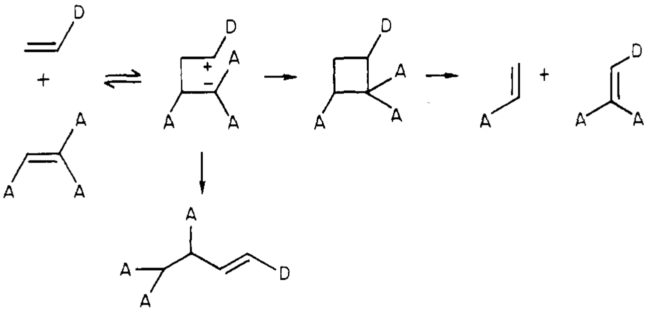
The reactions of *N*,*N*-dimethylvinylamine with electron-poor olefins have been studied. With 1,2-dicyanoethylene and *N*-phenylmaleimide, the cyclobutane adduct was obtained. Trimethyl ethylenetricarboxylate and tetramethyl ethylenetetracarboxylate yielded mostly an open-chain 1-butene derivative. At −90 °C reaction with trimethyl ethylenetetracarboxylate and subsequent treatment with alkylating agent yield the disalt of the 2:1 cyclohexane adduct and the salt of the metathesis product, the latter indicating the presence of cyclobutane at this temperature. We suggest that a zwitterionic intermediate can collapse to the cyclobutane, or rotate around the C_2–C_3 bond to form the 1-butene.

Introduction

Reactions of nucleophilic olefins such as enamines with olefins possessing varying electrophilic character give rise to various small molecule and polymer products. Hall and Ykman,[1] in their early study, reacted several vinylamines with trisubstituted electron-poor olefins. In certain conditions these isomerized to the thermodynamically favored 1-butene derivatives. Even uncatalyzed olefin metathesis was observed in a few cases. In these highly polar systems, the results were explained in the context of zwitterionic tetramethylene intermediates (Scheme I).

Cyclobutane formation from enamines has also been reported in the literature by Lewis and co-workers[2] in the reaction of *N*-isobutenylpyrrolidine with dimethyl fumarate, and by Fleming and Harley-Mason[3] in the reaction of *N*,*N*-dimethylisobutenylamine with acrylonitrile.

Scheme I[a]



[a] D = NR_2, OR, SR; A = CN, $COOCH_3$.

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[1] Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* 1975, *97*, 800.

[2] Lewis, F. D.; Ho, T. I.; DeVoe, R. J. *J. Org. Chem.* 1980, *45*, 5283.

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