Aromatic Nucleophilic Substitution. 21.[1] Electronic Structures of 1,3-Dinitro-4-phenanthryl Methyl Ether and the 4,4-Disubstituted 1,3-Dinitrophenanthrene Meisenheimer Complex

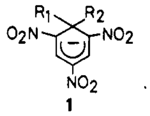
Shizen Sekiguchi,* Motohiko Hirai, Etsuro Ota,[2a] Hiroshi Hiratsuka,[2b] Yuji Mori,[2c] and Shigeyuki Tanaka[2d]

Department of Synthetic Chemistry, Gunma University, Kiryu, Gunma 376, Japan

Received March 1, 1985

The electronic structures of 1,3-dinitro-4-phenanthryl methyl ether (**2**) and its 4,4-dimethoxy-1,3-dinitrophenanthrene Meisenheimer complex (**3**), formed from **2** and $NaOCH_3$, were studied by UV-visible and NMR spectra and compared with the results calculated by a semiempirical Pariser-Parr-Paple method. The electronic transitions in the ether **2** and complex **3** were assigned to $^*\pi \leftarrow \pi$. Calculated transition energies and oscillator strengths agree well with the observed values. Calculations showed that in the S_0 state of complex **3** 90.3% of one negative charge donated by $^-OCH_3$ is distributed on the 1- and 3-NO_2 groups and that in the $S_1 \leftarrow S_0$ transition of the complex the π formal charge is further spread over the 1- and 3-NO_2 groups. A kinetic measurement in CH_3OH at 25 °C gave a little smaller equilibrium constant for formation of **3** than that for the similar naphthalene anionic σ complex.

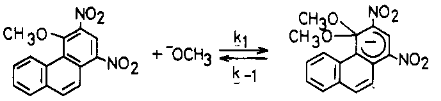
Many Meisenheimer complexes such as **1** have been prepared by nucleophilic attack on polynitro aromatic compounds (R_1 and R_2 are alkoxyl, hydroxyl, amino, cyano, and halo groups, etc.).[3] Such complexes have been identified as intermediates in many aromatic nucleophilic substitution reactions by means of improved reaction rate analyzers.[3]



1

Although the electronic structures of some such complexes have been theoretically analyzed by several workers,[4-8] no MO treatment has been performed on phenanthrene complexes.

Prior to a kinetic study on the formation and decomposition of the 4,4-dimethoxy anionic σ complex (**3**) in the reaction of 1,3-dinitro-4-phenanthryl methyl ether (**2**) and $NaOCH_3$, we have carried out MO calculations on **2** and **3**. In this reaction (eq 1) the hydrogen atom at the 5-position would be expected to exert a larger steric hindrance on the rate of formation of **3** than in similar reactions of benzene or naphthalene analogues.



2 **3** (1)

Table I. Calculated and Observed Transition Energies, Oscillator Strengths, and Transition Moments of 1,3-Dinitro-4-phenanthryl Methyl Ether 2

transition energy, eV			oscillator strength		transition moment	
$S_i \leftarrow S_0$	E_{calcd}	E_{obsd}	f_{calcd}	f_{obsd}	X	Y
			Method A			
S_1	3.446	*a*	0.010	*a*	0.157	0.092
S_2	3.482	3.580	0.533	*a*	−1.316	0.132
S_3	4.048	4.074	0.732	*a*	0.529	1.337
			Method B			
S_1	2.783	0.000	0.183	0.000	−0.293	0.816
S_2	2.880	0.000	0.514	0.000	−1.423	−0.121
S_3	3.318	3.580	0.504	*a*	0.312	1.300

[a] Not measured.

This paper reports on the electronic structures of **2** and **3** and on a comparison of the observed spectral results with those obtained by the MO method.

Method of Calculation

MO calculations were carried out by a semiempirical Pariser-Parr-Pople (PPP) method.[9,10] The geometries of **2** and **3** are shown in Figure 1.

The parameters used for PPP calculation were as follows: all C-C bond lengths and all bond angles, assumed to be 1.395 Å and 120°, respectively; the C-N and N-O bond lengths, assumed to be 1.486 and 1.210 Å. As one-center and two-center integrals, the Pariser-Parr[9,10] (eq 2) and the Nishimoto-Mataga (eq 3) equations[11] were used, respectively:

$$(ii/ii) = I_p - E_a \tag{2}$$

where i = 2p π AO (atomic orbital) of C-i, I_p = ionization potential, and E_a = electron affinity;

$$(ii/jj) = 1/(K + R_{ij}) \tag{3}$$

where i = 2p π AO of C-j and R_{ij} = internuclear distance between C-i and C-j.

---

(1) Part 20: Sekiguchi, S.; Hirai, M.; Tomoto, N. *J. Org. Chem.* **1984**, *49*, 2378.

(2) (a) College of Technology, Gunma University. (b) and (c) Tokyo Institute of Technology, Faculty of Science, Meguro, Tokyo 152. (d) Department of Applied Chemistry, Faculty of Engineering, the University of Tokyo, Hongo, Tokyo 113.

(3) (a) Pietra, F. *Q. Rev. Chem. Soc.* **1969**, *23*, 504. (b) de Boer, T. J.; Dirkx, I. P. "The Chemistry of the Nitro and Nitroso Groups", Part I; Feuer, H., Ed. Interscience: New York, 1969; p 487. (c) Crampton, M. R. *Adv. Phys. Org. Chem.* **1969**, *7*, 211. (d) Foster, R.; Fyfe, C. A. *Rev. Pure Appl. Chem.* **1966**, *16*, 61. (e) Buncel, E.; Norris, A. R.; Russel, K. E. *Q. Rev. Chem. Soc.* **1968**, *22*, 123. (f) Buck, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 120. (g) Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667. (h) Sekiguchi, S. *Yuki Gosei Kagaku Kyokai Shi* **1978**, *36*, 633. (i) Terrier, F. *Chem. Rev.* **1981**, *82*, 77.

(4) (a) Abe, T. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 508. (b) *Ibid.* **1966**, *39*, 627.

(5) Caveng, P.; Fisher, P. B.; Heilbronner, E.; Miller, A. L.; Zollinger, H. *Helv. Chim. Acta* **1967**, *50*, 848.

(6) (a) Hosoya, H.; Hosoya, S.; Nagakura, S. *Theor. Chim. Acta* **1968**, *12*, 117. (b) Nagakura, S. *Tetrahedron, Suppl.* **1963**, *19*, 361.

(7) Sekiguchi, S.; Tsutsumi, K.; Shizuka, H.; Matsui, K.; Itagaki, T. *Bull. Chem. Soc. Jpn.* **1967**, *49*, 1521.

(8) Sekiguchi, S.; Hirose, T.; Tsutsumi, K.; Aizawa, T.; Shizuka, H. *J. Org. Chem.* **1979**, *44*, 3921.

(9) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466, 767.

(10) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.

(11) Nishimoto, K.; Mataga, N. *Z. Phys. Chem.* (*Weisbaden*) **1957**, *12*, 335.

0022-3263/85/1950-5105$01.50/0

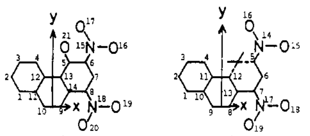


Figure 1. Geometry of **2** and **3** (positional number is available only for MO calculations and the substituent at the 5-position of **2** is assumed to be OH group).

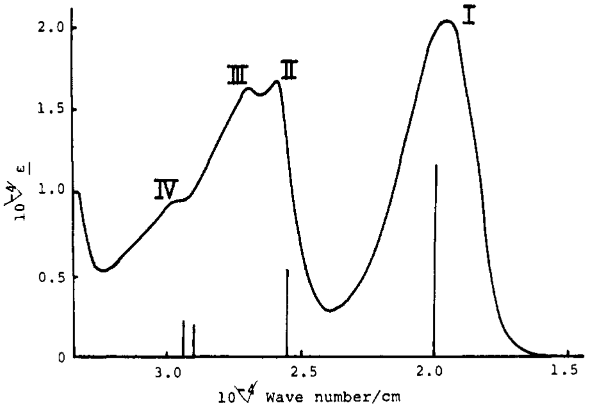


Figure 2. Absorption spectrum of **3** in CH_3OH: [**2**] = 4.37 × 10^{-5} M; [$NaOCH_3$] = 1.53 M; vertical lines, calculated oscillator strengths on an arbitary scale.

Table II. Calculated and Observed Transition Energies, Oscillator Strengths, and Transition Moments of Meisenheimer Complex 3

transition energy, eV			oscillator strength[a]		transition moment	
$S_i \leftarrow S_0$	E_{calcd}	E_{obsd}	f_{calcd}	f_{obsd}	X	Y
			Method A			
S_1	2.799	2.442	0.543 (1)	0.262 (1)	0.753	1.285
S_2	3.277	3.204	0.445 (0.83)	0.100 (0.38)	0.452	-1.171
S_3	3.733	3.416	0.369 (0.68)	0.140 (0.53)	0.964	-0.447
S_4	4.359	3.752	0.348 (0.64)	0.080 (0.31)	0.744	0.600
			Method B			
S_1	2.476	2.442	0.882 (1)	0.262 (1)	-0.354	-1.987
S_2	3.199	3.204	0.429 (0.49)	0.100 (0.38)	1.037	-0.676
S_3	3.607	3.416	0.141 (0.16)	0.140 (0.53)	0.371	-0.556
S_4	3.640	3.752	0.163 (0.18)	0.080 (0.31)	-0.706	-0.107

[a] The figures in parentheses represent the relative strengths.

In eq 3, K is determined so that the relationship $(ii/jj) = {}^1/_2[(ii/ii) + (jj/jj)]$ holds when $R_{ij} = 0$. The resonance integrals were assumed to be -2.38, -2.38, -2.30, and -2.38 eV for $\beta_{C=C}$, β_{CN}, β_{CO}, and $\beta_{N=O}$, respectively.

The following valence state ionization potentrals (I_p) and electron affinities (E_a) (eV) were used:

		C=	N	=O	O
method A[12]	I_p	11.16	24.80	17.70	33.00
	E_a	0.03	8.04	2.47	11.47
method B[13]	I_p	11.22	28.85	17.76	33.00
	E_a	0.62	12.26	3.87	11.47

The computation was carried out on a Hitachi M-280 located at the Tokyo Institute of Technology.

Results and Discussion

Absorption Spectrum of the Reaction of 1,3-Dinitro-4-phenanthryl Methyl Ether (2) with Sodium Methoxide in CH_3OH. Addition of excess $NaOCH_3$ to a methanolic solution of **2** at room temperature yielded a red solution instantly, indicating formation of an anionic σ complex (eq 1; Figure 2). Tables I and II show the calculated and observed transition energies, transition moments, and oscillator strengths in the electronic transitions of **2** and **3**. The absorption spectrum of **2** is comparatively simple, with a maximum absorption at 346 nm (28903 cm^{-1}, ε 7990), a shoulder band at 307 nm (32575 cm^{-1}, ε 9050), and no absorption above 430 nm (23256 cm^{-1}). The absorption spectra of **2** and **3** are attributable to $^*\pi \leftarrow \pi$ transitions, judging from the data in Tables I and II.

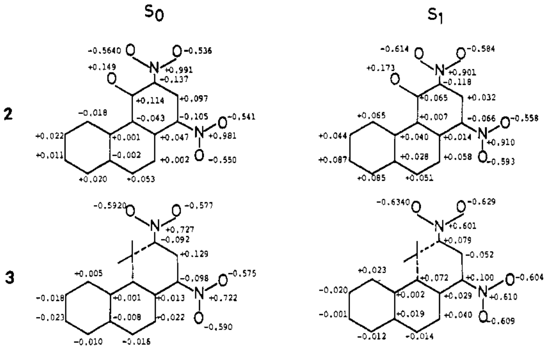


Figure 3. π formal charges of **2** and **3** in the S_0 and S_1 states.

Table III. π Formal Charge (S_0)[a]

pos[b]	**2** (method B)	**3** (method A)	pos[b]	**2** (method B)	**3** (method A)
1	0.023	-0.012	12	0.004	-0.040
2	0.011	-0.031	13	-0.050	0.024
3	0.025	-0.022	14	0.052	0.984
4	-0.022	0.000	15	0.746	-0.628
5	0.130	-0.221	16	-0.452	-0.637
6	-0.088	0.114	17	-0.492	0.987
7	0.114	-0.227	18	0.747	-0.627
8	-0.055	0.006	19	-0.459	-0.634
9	0.009	-0.019	20	-0.473	
10	0.061	-0.016	21	0.173	
11	-0.003	0.004			

[a] Compare the figures with those in Figure 3. [b] For positional numbers, refer to Figure 1. These numbers are available in the MO calculation only. Note that the positional numbers in the text were based on the normal method.

In Table I the observed transition energies (E_{obsd}) agree with the E_{calcd} values derived by method A better than those derived by method B. With **2** the spectrum did not show sharp absorptions so that the observed oscillator strengths (f_{obsd}) could not be measured accurately.

On the other hand, in Table II the E_{obsd} and f_{obsd} values for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions for **3** agree with the E_{calcd} and f_{calcd} derived by method B better than those derived by method A. The f_{obsd} values for the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ transitions, however, do not agree with the f_{calcd} derived by method A or B, which is a general result.[4-8] It seems that the parameters (I_p and E_a) of Hinze and Jaffé[12] are applicable to such a neutral species as **2**, while those of Ishidate and Nagakura[13] are applicable to such an ionic species as **3**.[6]

Absorption bands I–IV can be assigned to the $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$, $S_3 \leftarrow S_0$, and $S_4 \leftarrow S_0$ transitions, respectively (Table II, method B; Figure 2). Further, the E_{calcd} for the $S_3 \leftarrow S_0$ transition differs a little from its observed value (E_{obsd}), which may be attributed to the stabilization of the S_3 state of **3** by the solvent effect.

Figure 3 shows the π formal charges on **2** and **3** in the S_0 and S_1 states, in which the former was derived by method A and the latter by method B.

---

(12) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540.
(13) Ishidate, A.; Nagakura, S. *Theor. Chim. Acta* **1966**, *4*, 236.

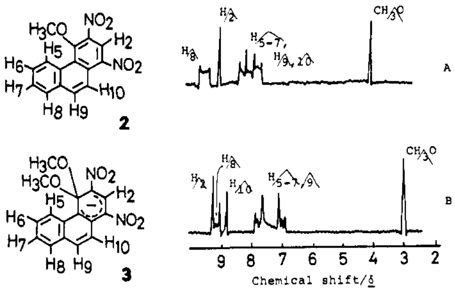


Figure 4. ^{1}H NMR spectra of **2** and **3** in Me_2SO-d_6: A, **2**; B, immediately after addition of 1 equiv of $NaOCH_3$.

The π formal charges of **2** and **3** calculated by both methods A and B differ only slightly from each other as shown for S_0 (Table III).

In the S_0 state of **2**, 4.4% of the total π formal negative charge is distributed on each of the 1- and 3-NO_2 groups (totaling 8.8%), while in the S_1 state 9.5 and 11.7% of the total π formal negative charge is distributed on the 1- and 3-NO_2 groups. Thus, in the $S_1 \leftarrow S_0$ transition of **2** more negative charge is spread over the 1- and 3-NO_2 groups.

A similar result was found in the $S_1 \leftarrow S_0$ transition of **3**: in the S_0 state of **3**, 17.0% of the total π formal negative charge is distributed on each of the 1- and 3-NO_2 groups (totaling 34.0%), and, interestingly, 9.7 and 90.3% of one negative charge donated by $^-OCH_3$ is distributed on all the ring carbons and the two NO_2 groups, respectively. Thus, the greater part of the negative charge donated is equally spread over the 1- and 3-NO_2 groups.

This spreading mode of the negative charge donated by $^-OCH_3$ is different to some extent from that of the 1,1-disubstituted naphthalene complex **5**.[8]

Further, in the $S_1 \leftarrow S_0$ transition of **3** (corresponding to band I in Figure 2) 23.2 and 25.5% of the total π formal negative charge is distributed on the 1- and 3-NO_2 groups, respectively, and the total π formal charge on all the ring carbons is positive. Therefore, it can be seen that more negative charge is spread from the ring carbons to the 1- and 3-NO_2 group in the $S_0 \leftarrow S_1$ transition of **3**.

NMR Spectra of the Reaction of 1,3-Dinitro-4-phenanthryl Methyl Ether (2) with Sodium Methoxide in Me₂SO. Figure 4 shows the time-dependent NMR spectra of the reaction of **2** with $NaOCH_3$. The signal (d–d) at δ 9.46 can be attributed to the H_8 proton rather than the H_5 proton (Figure 2, S_0 for **2**). Upon addition of $NaOCH_3$, the singlet at δ 4.05, attributed to the methoxy proton, was shifted upfield to δ 2.80, the peak strength corresponding to six protons. Such an upfield shift is seen in such naphthalene complexes as **5**.[3g] The downfield shift (δ 8.96 $\leftarrow$ 9.33) of the H_2 singlet corresponds well to the theoretical result; that is, the +0.097 → +0.129 change of the electron density at the 2-position (Figure 2; S_0 for **2** and **3**). Further, the H_8 signal was shifted upfield to δ 9.27 upon formation of **3**, corresponding to the +0.020 → −0.010 change of the electron density at the 2-position (Figure 2; S_0 for **2** and **3**). The doublet at δ 9.00 could be assigned to the H_{10} proton from consideration of the +0.002 → +0.022 change of the electron density at the 10-position (Figure 2; S_0 for **2** and **3**).

Kinetics and Equilibrium Constant. A kinetic measurement on the reaction shown in eq 1 was carried out at 25 °C in order to obtain the equilibrium constant. The rate is expressed by eq 4.[14,15] Since the dependence of k_ψ on $[NaOCH_3]$ was linear, k_1 and k_{-1} could be obtained from the slope and intercept (Table IV) and are compared with those of the benzene and naphthalene complexes in Table V.[15,16]

$$k_\psi = k_{-1} + k_1[^-OCH_3] \qquad (4)$$

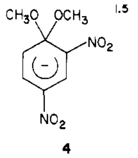
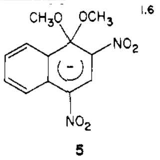
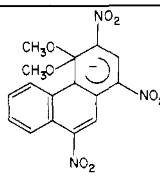
k_ψ: pseudo-first-order rate constant

Table IV. Rate and Equilibrium Constants for Formation of the Anionic σ Complex 3 in CH₃OH at 25 °C[a]

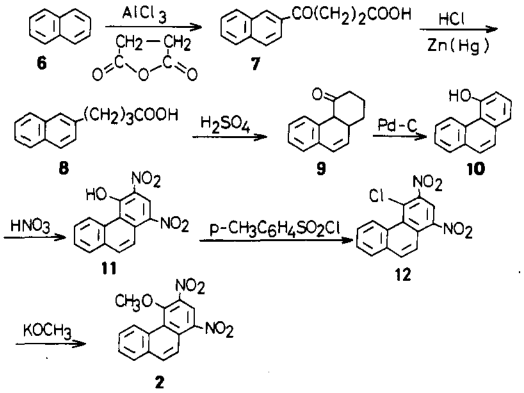
$10^3[NaOCH_3]$, M	10^3k_ψ, s^{-1}	k_1,[b] M^{-1} s^{-1}	10^3k_{-1},[b] s^{-1}	K_1[c]
2.31	1.42	0.178 ± 0.003	0.965 ± 0.079	186 ± 18
4.61	1.79			
6.92	2.18			
11.5	3.01			
23.1	4.99			
46.1	9.19			

[a] $[2]_0 = 4.37 \times 10^{-5}$ M; μ = 0.05 M ($NaClO_4$). [b] Calculated from eq 4. [c] $K_1 = k_1/k_{-1}$.

Table V. Rate and Equilibrium Constants for Formation of Various Anionic σ Complexes in CH₃OH at 25 °C

	 4 [15]	 5 [16]	 3
K_1, M^{-1}	2.74×10^{-5}	230	186 ± 18
k_1, M^{-1} s^{-1}	7.90×10^{-3}	0.9	0.178 ± 0.003
10^3k_{-1}, s^{-1}	28.7	3.95×10^{-3}	$(9.65 \pm 0.79) \times 10^{-4}$

Scheme I



The K_1 value for **3** is a little smaller than that for **5**, which results from a greater decrease in k_1 than in k_{-1}. We stated in previous work[8] that, in the $S_1 \leftarrow S_0$ transition of the complex, the more π formal negative charge that is spread from ring carbons to the nitro groups, the more stable the complex. In the $S_1 \leftarrow S_0$ transition of **5** the π formal negative charge on the 2- and 4-NO_2 groups increases from −0.6062 to −0.9039 (49.1% increase), while in the $S_1 \leftarrow S_0$ transition of **3** the charge on the 1- and 3-NO_2 groups increases from −0.885 to −1.265 (42.9% increase). These results correlate well with the difference between the K_1 values of **3** and **5**.

The smaller k_1 for **3** compared with **5** may be attributed to the steric hindrance exerted by H_5 against the approach of a nucleophile. Further, this difference could result from the higher potential energy of the transition state because of steric crowding of H_5, two methoxyl groups, and the

---

(14) Fendler, J. H.; Fendler, E. J.; Griffin, C. E. *J. Org. Chem.* **1969**, *34*, 689.

(15) Bernasconi, C. F. *J. Am. Chem. Soc.* **1968**, *90*, 4982.

(16) Fendler, E. J.; Fendler, J. H.; Byrne, W. E.; Griffin, C. E. *J. Org. Chem.* **1968**, *33*, 4141.

3-NO_2 group. It can be seen that **4** is far less stable than **5** and **3**, which is attributed largely to incomplete localization of the negative charge donated by $^-OCH_3$.

Experimental Section

General Procedures. Melting points are uncorrected. Elemental analyses were performed at the Microanalytical Center of Gunma University. Visible absorption spectra were measured with a Hitachi-124 UV-vis spectrophotometer. ^1H NMR spectra were taken with a Varian A-60 spectrometer. All reagents were purified by repeated recrystallization or by distillations.

Materials. The synthetic sequence for **2** is as shown in Scheme I.

4-Phenanthrol (10). Compound **10** was prepared by the sequence in Scheme I according to the method of Haworth.[17] Yields: **7**, 49%; **8**, 72%; **9**, 60%; **10**, 50%. Mp: **7**, 166.5–168.5 °C (lit.[17] mp 171–173 °C); **8**, 92.0–95.0 °C (lit.[17] mp 94–95 °C); **9**, 66.5–67.0 °C (lit.[17] mp 69 °C); **10**, 112.0–113.5 °C (lit.[17] mp 112.0–113.5 °C).

1,3-Dinitro-4-phenanthrol (11). To a stirred solution of 15 g (0.078 mol) of **10** and 900 mL of acetic acid was added dropwise 14.1 g of 70% HNO_3 (0.157 mol) at 60 °C with stirring, and the mixture was stirred for an additional 3 h. The mixture was poured onto ice water, and the precipitate was filtered, dried, and subjected to column chromatography (silica gel–benzene). When the benzene fraction was concentrated by distillation, 5.6 g (23%) of pure **11** crystallized: mp 189–190 °C (lit.[17] mp 205–208 °C).

4-Chloro-1,3-dinitrophenanthrene (12). A mixture of 5.6 g (0.02 mol) of **11**, 5.9 g (0.04 mol) of *N,N*-diethylaniline, and 3.8 g (0.02 mol) of *p*-toluenesulfonyl chloride was stirred at 80–90 °C for 8 h and then cooled to room temperature. After 300 mL of 1 N HCl was added, the mixture was stirred well, filtered, and dried. The residue was subjected to column chromatography (silica gel–benzene). After the benzene fraction was concentrated, 5.2 g (87%) of pure **12** crystallized out: mp 175.5–176.7 °C. Anal. Calcd for $C_{14}H_7ClN_2O_4$: C, 55.55; H, 2.33; N, 9.26. Found: C, 55.43; H, 2.34; N, 9.04.

1,3-Dinitro-4-phenanthryl Methyl Ether (2). A methanolic $KOCH_3$ solution (0.344 g, 0.0049 mol) was added dropwise to a 30-mL Me_2SO solution of 1 g (0.00328 mol) of **12** at room temperature; the mixture was stirred for 2 h and then poured onto 200 mL of ice water containing 2.5 mL of 2 N HCl. The precipitate was filtered, dried, and subjected to column chromatography (silica gel–benzene). After the benzene fraction was concentrated, recrystallization from ligroin yielded 0.82 g (83%) of pure **2**: mp 155.5–156 °C. Anal. Calcd for $C_{15}H_{10}N_2O_5$: C, 60.41; H, 3.38; N, 9.39. Found: C, 60.20, H, 3.36; N, 9.18.

Rate Measurement. The increase in the absorbance of **3** compared with that of **2** was measured at constant ionic strength ($NaClO_4$) with a molar excess of $NaOCH_3$ at 25 °C with a thermostated Union stopped-flow spectrophotometer RA-401 (Union Giken) in order to estimate the pseudo-first-order rate constant (k_ψ).

---

[17] Haworth, R. D. *J. Chem. Soc.* **1932**, 1125.

Proton Inventory of Phosphate Monoanion Catalyzed Hydrolysis of *S*-Ethyl Trifluorothioacetate

Jean M. Allen and K. S. Venkatasubban*

Department of Natural Sciences, University of North Florida, Jacksonville, Florida 32216

Received April 16, 1985

Dihydrogen phosphate monoanion ($H_2PO_4^-$) catalyzes the hydrolysis of *S*-ethyl trifluorothioacetate. In sodium dihydrogen phosphate solutions at pH 4.2 the only catalysts of concern are H_2O and $H_2PO_4^-$. The kinetic solvent isotope effects (k_H/k_D) on the water and $H_2PO_4^-$ catalyzed hydrolysis are 2.86 and 2.00, respectively. The observed isotope effects suggest a general base mechanism for both water and $H_2PO_4^-$ catalyzed hydrolysis. In mixtures of H_2O and D_2O, the water catalyzed hydrolysis shows a nonlinear dependence on the atom fraction of deuterium, *n*. This nonlinear dependence is consistent with a three-proton model for the transition state. The $H_2PO_4^-$ catalyzed hydrolysis shows a linear dependence on *n*. This linear dependence is consistent with a one-proton model for the transition state in which a single proton is responsible for the entire observed solvent isotope effect.

The general base catalyzed hydrolysis of *S*-ethyl trifluorothioacetate is well established. Acetate ion, imidazole, and phosphate mono- and dianions are all known to function as general bases in the above reaction.[1] In an effort to define the transition state structures for such a general base catalyzed reaction in greater detail, we have conducted a proton-inventory study of the phosphate monoanion catalyzed hydrolysis of ethyl trifluorothioacetate. The results are reported herein.

Results

The pseudo-first-order rate constants for the monoanion catalyzed hydrolysis were measured in sodium dihydrogen phosphate solutions at pH 4.2. At this pH the only catalysts we need to consider are $H_2PO_4^-$ ion and water. The water reaction is independent of pH between pH 2 and 7, and phosphate exists exclusively in the monoanionic form at this pH. The three pK_a values for H_3PO_4 are 2.12, 7.21, and 12.32, respectively.[2] Table I lists the observed first-order rate constants for different phosphate mo-

Table I. First-Order Rate Constants for the Hydrolysis of *S*-Ethyl Trifluorothioacetate in NaH_2PO_4 Solutions at pL 4.20[a] at Different Atom Fractions of Deuterium at 30 ± 0.1 °C (Ionic Strength = 1.0 M with NaCl)

n, atom fraction deuterium	10^3k_{obsd},[b] s^{-1} (NaH_2PO_4, M)
0	11.2 (0.50), 11.0 (0.46)[c], 10.5 (0.40), 10.1 (0.37),[c] 9.6 (0.30), 9.6 (0.28), 9.3 (0.20), 9.0 (0.18),[c] 8.5 (0.10), 8.5 (0.09)[c]
0.245	9.2 (0.50), 8.7 (0.40), 8.0 (0.30), 7.8 (0.20), 6.8 (0.10)
0.495	7.2 (0.50), 6.9 (0.40), 6.4 (0.30), 5.9 (0.20), 5.3 (0.10)
0.800	5.4 (0.50), 5.1 (0.40), 4.3 (0.20), 3.8 (0.10)
0.990	4.3 (0.50), 4.0 (0.40), 3.8 (0.30), 3.3 (0.20), 3.0 (0.10)

[a] pL = pH or pD; reported values are uncorrected pH meter readings. [b] Mean of 3–5 determinations, reproducible within about 3%. [c] Rate constants measured at pH 3.15.

---

[1] Fedor, L. R.; Bruice, T. C. *J. Am. Chem. Soc.* **1965**, *87*, 4138.

0022-3263/85/1950-5108$01.50/0