Meisenheimer Complexes. A Kinetic Analysis of the Behavior of 2,4-Dinitro-5-methoxythiophene and -selenophene in Methanol

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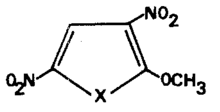
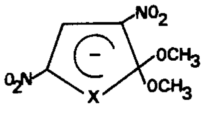
Received April 15, 1975

The kinetics of the formation and decomposition of the *gem*-dimethoxyl Meisenheimer-type complexes **2a**, **2b** (X = S, Se) derived from 2,4-dinitro-5-methoxythiophene and -selenophene (**1a**, **1b**, X = S, Se) has been studied in methanol. The pH–rate profiles of these reactions allowed determination of rate coefficients for attack of either methoxide ion or methanol on **1a** and **1b** as well as those for the decomposition of adducts **2a** and **2b**, whether it is in a spontaneous process or indirectly with the aid of a solvated proton. The rate of the attack of methoxide ion on **1a** and **1b** has also been measured at different temperatures in dilute potassium methoxide solutions which provides energies and entropies of activation for this reaction. The results are compared with previously reported data for the formation and decomposition of the adduct **4** derived from 2,4,6-trinitroanisole (**3**). The selenophenic complex **2b** appears to be the most stable Meisenheimer *gem*-dimethoxyl adduct yet observed in methanol.

The reaction of methoxide ion with nitro derivatives of benzene, pyridine, and pyrimidine often results in the formation of stable adducts, referred as to Meisenheimer complexes.[1] Recent rapid kinetic studies have allowed the determination of kinetic and thermodynamic parameters for the formation and decomposition of a great number of such complexes, thus leading to a better understanding of the mechanism of these processes.[2-5] The formation of similar adducts from various five-membered ring substrates such as 2,4-dinitro-5-methoxythiophene and -selenophene (**1a**, **1b**, X = S, Se) has also been reported.[6,7] In this case, the thermodynamic stability of the corresponding complexes **2a**, **2b** (X = S, Se) is so high that they are partially formed in pure methanol and only an order of magnitude could be obtained for the parameters of the reactions. We now report a comprehensive kinetic analysis of the behavior of **1a**, **1b** in pure methanol.





1a X = S 2a

1b X = Se 2b

Results

The reaction of methoxide ion with 2,4-dinitro-5-methoxythiophene (**1a**) and -selenophene (**1b**) in methanol results in the immediate formation of the red-colored adducts **2a** and **2b** which show an absorption band at 530 nm (ϵ_{2a} 22,800 M^{-1} cm^{-1}; ϵ_{2b} 21,000 M^{-1} cm^{-1}). At this wavelength the parent molecules have zero or negligible absorption. Both adducts, which were identified by NMR spectroscopy,[6,7] are completely formed in a solution with methoxide ion concentration as low as 5×10^{-4} M. Therefore, it was necessary to use buffer solutions to carry out a comprehensive study of their formation and decomposition. The buffer solutions were prepared from various carboxylic acids and phenols AH and, in general, were made up so as to give a total ionic strength of 0.01 M from the buffer species A^- alone without any added neutral salt. This low ionic strength μ was chosen because, as previously shown by electrochemical measurements in methanol,[8] the mean activity coefficient $\gamma\pm$ can then be calculated by using a simplified Debye–Hückel type equation ($\log \gamma\pm = -Bz^2\sqrt{\mu}$), thus allowing the hydrogen ion concentration $[H^+]$ of the solutions to be deduced from the measured activity (H^+) of the solvated proton. The pH values were determined as previously described[8] and are relative to the standard state in methanol. Using the same buffer at different ionization ratios $[A^-]/[AH]$, we were able to cover a range from pH 5.48, which is the value for the dichloracetate–dichloracetic acid buffer ($[A^-]/[AH] = 1/3$), to 13.70, which is that for the *p*-chlorophenoxide–*p*-chlorophenol buffer ($[A^-]/[AH] = 3$) and close to the pH value of a potassium methoxide solution 5×10^{-4} M at the same ionic strength 0.01 M (NaBr added).

Plotting the variations at 530 nm of the optical density obtained at equilibrium as a function of pH, we observed that the adducts **2a** and **2b** are half formed at pH 11.16 and 9.86, respectively. Taking into account the relatively high value of the Debye–Hückel coefficient B in methanol (B = 1.80),[8] these $pH_{1/2}$ values are identical with the pK_a values for the formation of adducts (eq 1) at μ = 0.01 M and are related to the thermodynamic pK_a values at zero ionic strength by eq 2.

$$1 + CH_3OH \rightleftarrows 2 + H^+ \quad K_a = \frac{(2)(H^+)}{(1)} \tag{1}$$

$$pK_a = pH_{1/2} - \log \frac{\gamma_2}{\gamma_1} \tag{2}$$

Assuming $\gamma_1 \simeq 1$, which is here a quite reasonable assumption, these latter were therefore determined by a Debye–Hückel extrapolation from similar $pH_{1/2}$ measurements at $\mu = 2.5 \times 10^{-3}$, 5×10^{-3}, and 2×10^{-2} M. The following values were so obtained.

$$pK_a^{2a} = 11.36 \pm 0.03 \qquad pK_a^{2b} = 10.07 \pm 0.03$$

Indeed, in the case of the thiophenic adduct **2a**, the value is not very different from that roughly estimated by Illuminati et al.[6b]

Using the stopped-flow method as well as conventional methods, we were able to follow spectrophotometrically the kinetics of formation and/or the decomposition of adducts **2a**, **2b**. For adduct formation measurements were made by mixing solutions of the substrates with appropriate buffers or with dilute potassium methoxide solutions. Experimental data for adduct decomposition were similarly obtained by mixing solution of adducts in very dilute potassium methoxide solutions (5×10^{-4} M) with the more acidic buffer solutions. The appearance or fading of color was in all cases a first-order process. The logarithm of the observed first-order rate constant k_{obsd} for the combined for-

Table I
Buffer Influence on the Kinetics of Formation and Decomposition of 2a, 2b[a]

Total buffer concn	4-Cyanophenoxide buffer $[A^-]/[AH] = 1$ pH = 11.72 k_{obsd}, sec^{-1}		Dichloracetate buffer $[A^-]/[AH] = 1$ pH = 5.96 k_{obsd}, sec^{-1}	
$[A^-] + [AH]$	**2a**	**2b**	**2a**	**2b**
5×10^{-3}	$3.59 \pm 0.10 \times 10^{-4}$	$9.05 \pm 0.25 \times 10^{-4}$	$1.71 \pm 0.06 \times 10^{-2}$	$5.05 \pm 0.15 \times 10^{-3}$
10^{-2}	$3.55 \pm 0.10 \times 10^{-4}$	$9.35 \pm 0.25 \times 10^{-4}$	$1.61 \pm 0.06 \times 10^{-2}$	$4.80 \pm 0.15 \times 10^{-3}$
1.5×10^{-2}	$3.57 \pm 0.10 \times 10^{-4}$	$9.25 \pm 0.25 \times 10^{-4}$	$1.70 \pm 0.06 \times 10^{-2}$	$5.26 \pm 0.15 \times 10^{-3}$
2×10^{-2}	$3.42 \pm 0.10 \times 10^{-4}$	$9.40 \pm 0.25 \times 10^{-4}$	$1.64 \pm 0.06 \times 10^{-2}$	$5.00 \pm 0.15 \times 10^{-3}$

[a] 20°; $\mu = 0.01\,M$.

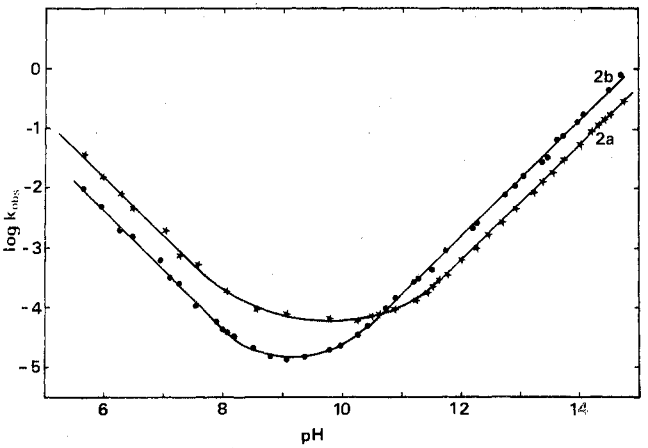


Figure 1. The pH dependence of k_{obsd} (sec^{-1}) for the formation and decomposition of adducts **2a, 2b** in methanol: 20°, $\mu = 0.01\,M$.

mation and decomposition of complexes **2a, 2b** are plotted in Figure 1 as a function of pH. The data in Table I show that variation of buffer concentration at constant pH does not significantly affect the value of k_{obsd} within experimental error, indicating the absence of catalysis by buffer, at least at the low concentrations used. In addition, smooth pH–rate profiles are obtained despite the fact that buffers of varying chemical types were used, which clearly indicates, as expected in methanol, that buffer species (particularly phenoxide anions) do not react with the substrates.[9]

The observed rate constant k_{obsd} reflects the rate of approach to equilibrium between the substrates **1** and the corresponding adducts **2** and is the sum of the pseudo-first-order rate constants k_f and k_d, respectively, for the formation and decomposition of **2**.

$$k_{obsd} = k_f + k_d \qquad (3)$$

At equilibrium

$$k_f[1] = k_d[2] \qquad (4)$$

so that k_f and k_d are related to the equilibrium constant K_a by the relation 5 and consequently with the experimental $pH_{1/2}$ value corresponding to the half-formation of adducts **2**.

$$\frac{k_f}{k_d} = \frac{K_a\gamma_1}{(H^+)\gamma_2} = \frac{(H^+)_{1/2}}{(H^+)} \qquad (5)$$

Combining eq 3 and 5 leads to

$$k_d = \frac{k_{obsd}}{1 + (H^+)_{1/2}/(H^+)} \qquad (6)$$

$$k_f = \frac{k_{obsd}}{1 + (H^+)/(H^+)_{1/2}} \qquad (7)$$

Some typical values of k_f and k_d calculated from eq 6 and 7 are given in Table II for the selenophenic adduct. Complete

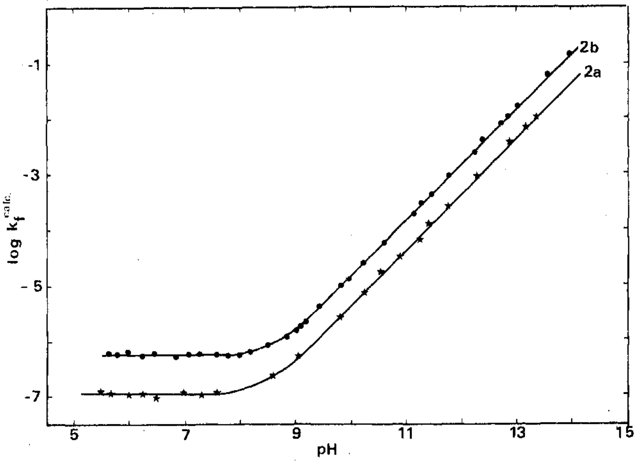


Figure 2a. The pH dependence of k_f (sec^{-1}) for the formation of adducts **2a, 2b** in methanol: 20°, $\mu = 0.01\,M$.

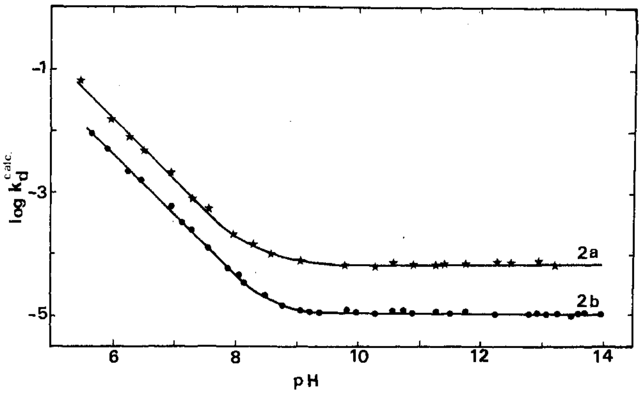


Figure 2b. The pH dependence of k_d (sec^{-1}) for the decomposition of adducts **2a, 2b** in methanol: 20°, $\mu = 0.01\,M$.

data are graphically represented in Figure 2, showing the pH dependence of k_f and k_d.

The observed pH–rate profiles are consistent with equations of the form

$$k_f = k_1^{CH_3OH} + k_2[CH_3O^-] = k_1^{CH_3OH} + \frac{k_2K_s}{(H^+)\gamma\pm} \qquad (8)$$

(K_s = autoprotolysis constant of methanol, $10^{-16.86}$ at 20°[8])

$$k_d = k_{-1}[H^+] + k_{-2} = \frac{k_{-1}(H^+)}{\gamma\pm} + k_{-2} \qquad (9)$$

$$k_{obsd} = \frac{k_{-1}(H^+)}{\gamma\pm} + k_{-2} + k_1^{CH_3OH} + \frac{k_2K_s}{(H^+)\gamma\pm} \qquad (10)$$

and then with the following general scheme where the adducts **2** may be formed by attack of either methoxide ion (second-order rate constant k_2) or methanol (first-order rate constant $k_1^{CH_3OH}$) on the parent ethers **1**, and may de-

Table II
Experimental and Calculated Pseudo-First-Order Rate Constants k_{obsd}, k_f, k_d for the Formation and/or Decomposition of the Selenophenic Adduct 2b in Methanol[k]

pH	$k_{obsd} \times 10^4$, sec^{-1}	$k_f \times 10^4$, sec^{-1}	$k_d \times 10^4$, sec^{-1}	pH	$k_{obsd} \times 10^4$, sec^{-1}	$k_f \times 10^4$, sec^{-1}	$k_d \times 10^4$, sec^{-1}
5.66[a]	93	5.86×10^{-3}	93	10.88[f]	1.36	1.24	0.110
5.96[a]	50	6.20×10^{-3}	50	11.24[g]	2.73	2.60	0.109
6.26[a]	19	4.80×10^{-3}	19	11.48[f]	4.4	4.29	0.103
6.44[a]	15.6	5.91×10^{-3}	15.6	12.18[g]	19.3	19.2	0.092
7.09[b]	3.20	5.45×10^{-3}	3.20	12.26[h]	26.4	26.3	0.105
7.27[b]	2.56	6.50×10^{-3}	2.56	12.75[h]	75.3	75.2	0.097
7.57[b]	1.12	5.75×10^{-3}	1.12	12.89[i]	108	108	0.100
7.87[b]	0.56	5.7×10^{-3}	0.56	13.04[h]	147	147	0.097
8.05[b]	0.42	6.5×10^{-3}	0.42	13.46[j]	317	317	0.080
8.48[c]	0.22	9×10^{-3}	0.21	13.58[j]	605	605	0.110
8.78[c]	0.16	1.21×10^{-2}	0.145	13.70[i]	740	740	0.107
9.04[d]	0.13	1.68×10^{-2}	0.11	13.98[j]	1400	1400	0.106
9.34[d]	0.14	3.22×10^{-2}	0.107	14.08[j]	1780	1780	0.107
9.95[e]	0.23	0.13	0.104	14.46[j]	4500	4500	0.112
10.25[e]	0.345	0.245	0.100	14.68[j]	7700	7700	0.115

[a] Buffers used were a, dichloracetate; b, salicylate; c, *m*-chlorobenzoate; d, benzoate; e, 2,4,6-trichlorophenoxide; f, 2,6-dichlorophenoxide; g, 4-cyanophenoxide; h, 2-bromophenoxide; i, 4-chlorophenoxide. [j] Potassium methoxide solutions 6×10^{-4}–10^{-2} *M*. [k] 20°, $\mu = 0.01$ *M*.

compose either in a spontaneous process (first-order rate constant k_{-2}) or indirectly with the aid of H^+ (second-order rate constant k_{-1}).

$$1 + CH_3OH \underset{k_{-1}}{\overset{k_1^{CH_3OH}}{\rightleftharpoons}} 2 + H^+$$

$$1 + CH_3O^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2$$

At high pH, eq 8 and 9 simplify to eq 8a and 9a

$$k_f \simeq k_2[CH_3O^-] = \frac{k_2K_s}{(H^+)\gamma\pm} \tag{8a}$$

$$k_d \simeq k_{-2} \tag{9a}$$

thus leading to a straight line of slope +1 and a plateau, respectively, in Figures 2a and 2b and allowing an easy determination of values of k_2 and k_{-2}. At low pH, eq 8 and 9 reduce similarly to eq 8b and 9b.

$$k_f \simeq k_1^{CH_3OH} \tag{8b}$$

$$k_d \simeq k_{-1}[H^+] = \frac{k_{-1}(H^+)}{\gamma\pm} \tag{9b}$$

Another plateau and straight line of slope −1 from which one can obtain values for $k_1^{CH_3OH}$ and k_{-1} is shown in Figures 2a and 2b. Table III summarizes the various rate coefficients so obtained.

Considering these values, the observed first-order rate constant k_{obsd} is expected to be identical with k_d and k_f at low and high pH, respectively, which is in agreement with the experimental observation. In the intermediate pH range, values of the terms $k_2K_s/(H^+)\gamma\pm$ and/or $k_{-1}(H^+)/\gamma\pm$ cannot be neglected relative to the sum $k_{-2} + k_1^{CH_3OH}$ so that no plateau appears in the experimental pH-rate profile.

We studied also the formation of adducts at different temperatures in dilute solutions of potassium methoxide 5×10^{-4}–10^{-2} *M*. The ionic strength was maintained constant at 0.01 *M* by adding NaBr as necessary. In this case, only the reaction

$$1 + CH_3O^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2$$

occurs and the expression for the observed first-order rate constant k_{obsd} reduces to

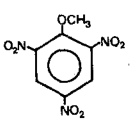
$$k_{obsd} = k_{-2} + k_2[CH_3O^-] \tag{11}$$

Plots of k_{obsd} against the methoxide ion concentration gave good straight lines whose slopes are k_2 and intercepts k_{-2}. As could be expected from the data previously obtained in the buffer solutions, the intercepts were negligible in all cases and did not allow the estimation of k_{-2}. Therefore, only k_2 values are given in Table III. As can be seen, the value obtained for k_2 at 20° agrees nicely with that determined at the same temperature from the pH-rate profile of Figure 2, thus justifying calculation of the mean activity coefficient $\gamma\pm$ by means of the simplified Debye-Hückel equation.[8] Activation parameters calculated from Arrhenius plots of log k_2 vs. $1/T$ are given in Table IV with analogous data reported for the 1,1-dimethoxy adduct **4** derived from 2,4,6-trinitroanisole (**3**).[2b]

Table III
Specific Rate Constants for the Formation and Decomposition of Complexes 2a, 2b in Methanol[d]

		2a	2b	4
k_2, M^{-1} sec^{-1}	10°	15.8[a]		
	20°	28.2,[a] 26.3[b]	71,[a] 69[b]	11.8[c]
	30°	55[a]	148[a]	
	40°	104[a]	295[a]	
k_{-2}, sec^{-1}	20°	7.8×10^{-5} [b]	1.04×10^{-5} [b]	6.05×10^{-4} [c]
$k_1^{CH_3OH}$, sec^{-1}	20°	10^{-7} [b]	5.75×10^{-7} [b]	
k_{-1}, M^{-1} sec^{-1}	20°	1.05×10^4 [b]	2.65×10^3 [b]	$\sim 4.5 \times 10^3$

[a] From measurements in potassium methoxide solutions. [b] From measurements in buffer solutions. [c] Calculated from data of ref 2b. [d] $\mu = 0.01$ *M*.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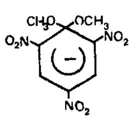
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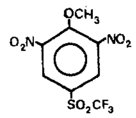
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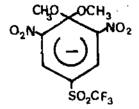
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Discussion

The rate of methoxide ion attack on carbon carrying the methoxy group of 2,4-dinitro-5-methoxyselenophene (**1b**) is about 2.5-fold faster than that on the similar carbon of

Table IV
Kinetic and Activation Parameters for the Formation of Complexes 2a, 2b in Methanol at 25°[c]

	2a	2b	4
k_2, M^{-1} sec^{-1}	40.7, 36[a]	102	17.3[b]
$\Delta H_2^{\ddagger}$, kcal mol^{-1}	9.9 ± 0.6	12.2 ± 0.6	12.9 ± 1[b]
$\Delta S_2^{\ddagger}$, eu	−17.8 ± 2.3	−8.4 ± 2.3	−9.4 ± 3.4[b]
$\Delta G_2^{\ddagger}$, kcal mol^{-1}	15.2 ± 1.3	14.7 ± 1.3	15.7 ± 2[b]

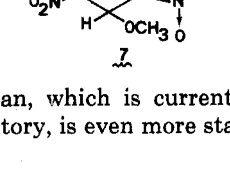
[a] Reference 6b. [b] Reference 2b. [c] μ = 0.01 M.

2,4-dinitro-5-methoxythiophene (**1a**). Although the contribution of the corresponding reaction to the formation of adducts appears to be experimentally negligible, the rate constant for attack of methanol on **1b** is found to be fivefold greater than that for attack on **1a**. These results agree well with the general features reported by Spinelli, Dell'Erba, and coworkers[10,11] for a similar nucleophilic attack of thiophenoxide and selenophenoxide anions and thus confirm the higher reactivity of selenophenic substrates toward nucleophilic reagents.

Considering especially the formation of adducts from methoxide ion attack on **1a**, **1b**, inspection of Table IV is indeed very instructive. As can be seen, the enthalpy of activation for the formation of **2a** is 2.3 kcal mol^{-1} lower than that for the formation of **2b**. Consequently, this latter is kinetically favored only because the corresponding entropy of activation is significantly less negative (by about 10 cal deg^{-1} mol^{-1}) than that associated with the thiophenic complex formation, suggesting that the transition state for the formation of **2b** is less solvated than that for **2a**.

In addition to its slower formation, **2a** decomposes more rapidly than **2b**, whether spontaneously or via the aid of H^+. Consequently, the selenophenic adduct appears to be thermodynamically 20-fold more stable than the thiophenic analog. This situation is, indeed, similar to one we have recently encountered by comparing the stabilities of monomethoxyl complexes resulting from the reaction of methoxide ion with 2,4-dinitrothiophene and selenophene.[21]

In Meisenheimer complex chemistry, 2,4,6-trinitroanisole (**3**) has been used very often as a reference for comparison of reactions involving the formation and decomposition of *gem*-dimethoxy Meisenheimer-type adducts.[1,2b,3b,4] As shown in Table III, the trinitro complex **4** is thermodynamically much less stable than the adducts **2a** and **2b** ($pK_a^{2a} - pK_a^{4} = -1.23$; $pK_a^{2b} - pK_a^{4} = -2.53$), the stability difference arising essentially from its significantly faster rate of spontaneous decomposition: $k_{-2}^{4}/k_{-2}^{2a} = 7.7$; $k_{-2}^{4}/k_{-2}^{2b} = 58$. In contrast, the stability of **2a**, **2b** is close to that of the 1,1-dimethoxy complex **6** formed from 4-trifluoromethylsulfonyl-2,6-dinitroanisole (**5**):[12] $pK_a^{2a} - pK_a^{6} = +0.48$; $pK_a^{2b} - pK_a^{6} = -0.82$. Evidently, **2b**, **6**, and **2a** are, in this order, the most stable *gem*-dimethoxy complexes which have been observed to form in methanol. It must be noted, however, that another Meisenheimer complex, namely the monomethoxy adduct **7** formed from 4,6-dinitrobenzofuroxan, which is currently under investigation in this laboratory, is even more stable than **2a** and **2b**: $pK_a^{7} = 6.46$.[13]



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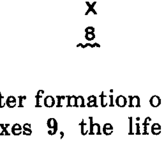
Because of their high stability, demonstrated by the pK_a values which are not too far from the pH value of pure methanol, formation of **2a** and **2b** from the parent molecules **1a** and **1b** can be observed in the absence of any added methoxide. Dissolving 10^{-3} M substrates **1** in methanol results in the slow development of an absorption at 530 nm which is rather weak in the case of X = S but more intense in the case of X = Se. In addition, adding an equimolar amount of potassium methoxide and eliminating the solvent allows the adducts **2a** and **2b** to be isolated as crystalline potassium salts which are very explosive, especially **2b**. Good elemental analyses have been obtained for these solids, which also have NMR spectra identical with those previously recorded by studying the reactions in situ.[5,6]

The factors governing the stability of 1,1-*gem*-dimethoxy complexes formed from 2,4,6-trinitroanisole as well as various substituted 4-X-2,6-dinitroanisoles have been extensively discussed.[1,2b,3b,14] According to recent suggestions the release of steric strain which exists around the carbon bearing the methoxy group[15,2b] would play a major role in contributing to the stability of 1,1 complexes, together with the stabilizing influence of the two methoxy groups on their tetrahedral carbon and the capacity of the electron-withdrawing substituents to delocalize their negative charge. In considering the adducts **2a** and **2b**, a comparison with a benzene analog such as **4** is interesting. Whereas the influence of alkoxy substitution at the sp^3 carbon as well as delocalization of the negative charge by the electron-withdrawing substituents can similarly account for the stability of **2a** and **2b**, their formation involves less release of steric strain around the methoxy group of parent molecules **1a** and **1b**. Also, whereas the C_2–C_1–C_6 angle in the anisoles is almost 120°, crystallographic studies[17,18] have shown that the S–C_2–C_3 and Se–C_2–C_3 angles of the thiophene and selenophene derivatives are equal to 111°50′ and 110°40′, respectively, values which are close to that for a tetrahedral carbon. Consequently, as previously noted by Illuminati et al.,[6b] the formation of **2a**, **2b** involves less bond strain than that of **4**. In addition to these steric and geometrical differences, it should also be noted that the measured pK_a values are dependent not only on the stability of the formed adducts but also on that of the starting materials; and with respect to this latter point, one may reasonably expect the ground-state energy level of 2,4-dinitro-5-methoxythiophene and -selenophene to be higher than that of 2,4,6-trinitroanisole. Consequently, it is clear that any attempt to appreciate the contribution of each of these individual factors to the increased stability of **2a**, **2b** relative to that of **4** would be unrealistic.

In the case of substituted 4-X-2,6-dinitroanisoles, the appearance of 1,1 complexes **8** is often preceded by the



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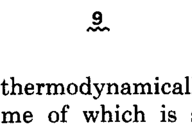

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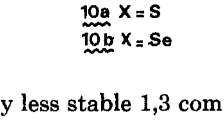

10a X = S
10b X = Se

faster formation of thermodynamically less stable 1,3 complexes **9**, the lifetime of which is strongly increased in Me_2SO.[2b,3b,4,14] Analogous to these results, it might be expected that methoxide ion attack would also occur initially on the unsubstituted 3 carbon of **1a**, **1b**, leading to complexes **10a**, **10b**. Despite careful NMR and kinetic investigations, we were not able to identify such complexes in methanol–Me_2SO mixtures regardless of the Me_2SO and base concentration. Indeed, the fact that complexes **10a**,

10b are not formed prior to **2a, 2b** is not really surprising, since it is known that the β position of thiophenic and selenophenic derivatives is less sensitive to nucleophilic attack than the α position.[19] Furthermore, recent kinetic studies have shown that the rate of methoxide ion attack on the 5-unsubstituted carbon of 2,4-dinitrothiophene and -selenophene is somewhat slower than that on the analogous 5 carbon bearing the methoxy group of **1a, 1b**.[20,21] This behavior, which contrasts strongly with that observed in benzenic and pyridinic series,[1,3,4] will be discussed in a forthcoming paper.

Experimental Section

Materials. 2,4-Dinitro-5-methoxythiophene was prepared by nitration of 2-methoxy-5-nitrothiophene according to the method described by Illuminati et al.,[6b] mp 140°. 2,4-Dinitro-5-methoxyselenophene was prepared by dissolving 3 g of 2-bromo-3,5-dinitroselenophene in 30 ml of methanol. To this stirred solution was added dropwise at −40° 15 ml of methanolic potassium methoxide (1 *M*). The mixture was allowed to stand for 30 min at −20° and then poured into 200 ml of hydrochloric acid (2 *N*) and extracted with ether. The ether phase was washed with water, dried, and evaporated. The dinitro compound was recrystallized from chloroform, mp 119°. Anal. Calcd for $C_5H_4N_2O_5Se$: C, 23.90; H, 1.59; N, 11.16. Found: C, 23.70; H, 1.70; N, 11.21.

Potassium 2,2-dimethoxy-3,5-dinitrothia- and -selenacyclopentenates (**2a, 2b**) were prepared by addition of nearly 1 equiv of 1 *M* methanolic potassium methoxide to a solution of the parent molecules **1a, 1b** (100 mg) in a minimum amount of methanol. The reaction mixture turned immediately reddish purple and was allowed to stand at room temperature for 15 min. Then the solvent was removed under vacuum and the residues, collected as purple solids, were washed with anhydrous ether and dried under vacuum to constant weight in order to eliminate any associated solvent.

Anal. Calcd for $C_6H_7N_2KO_6S$: C, 26.26; H, 2.57; N, 10.25; S, 11.68. Found: C, 26.20; H, 2.72; N, 10.18; S, 11.41. Calcd for $C_6H_7N_2KO_6Se$: C, 22.43; H, 2.19; N, 8.72. Found: C, 22.84; H, 2.09; N, 8.64.

Methanol and methanolic potassium methoxide solutions were prepared as previously described.[8a] The various buffers used for the rate measurements were purified according to classical methods.

Rate and pH Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained to ±0.5°. Other kinetic measurements were made using a Beckman spectrophotometer. All kinetic runs were carried out under pseudo-first-order conditions with a substrate concentration of about 3×10^{-5} *M*. Rate constants are accurate to ±3%.

The pH of buffer solutions and dilute potassium methoxide solutions has been measured according to a method previously reported by using an hydrogen electrode.[8] The pH values so obtained are relative to the standard state in methanol.

Registry No.—**1a,** 27357-00-2; **1b,** 36658-93-2; **2a,** 55955-40-3; **2b,** 55955-41-4; 2-bromo-3,5-dinitroselenophene, 17580-53-9; potassium methoxide, 865-33-8.

References and Notes

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(9) In order to check more carefully the possibility that phenoxide ions may attack **1a, 1b** to yield a complex, some experiments have been carried out at a higher ionic strength ($\mu = 5 \times 10^{-2}$ *M*) with two different buffer systems, namely the *p*-cyanophenoxide–*p*-cyanophenol buffer ($|A^-|/|AH| = \frac{1}{2}$, pH 11.20) and the 2,6-dichlorophenoxide–2,6-dichlorophenol buffer ($|A^-|/|AH| = 1.75$, pH 11.20). Increasing the concentration of the basic species from 10^{-2} to 5×10^{-2} and adding NaBr as necessary still does not significantly affect k_{obsd} within experimental error. It is thus clear that phenoxide ions do not attack **1a, 1b** and that no appreciable buffer catalysis of the formation of **2a, 2b** occurs under our experimental conditions. Another evidence is, indeed, the fairly good agreement observed between the k_2 values determined separately from measurements in buffer solutions and dilute potassium methoxide solutions.

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