scribed previously.[1] NaOH solutions were prepared from Titrisol.

Kinetic determinations were made on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained to ±0.5 °C. All runs were carried out under first-order conditions with a substrate concentration of about 5×10^{-5} M. Rate constants are considered accurate to ±3%.

Acknowledgment. The authors thank the North Atlantic Treaty Organization for a grant (NATO Res. 1540) to F.T. and M.J.S. supporting this research.

Registry No. **1a**,H^+, 56776-17-1; **1b**,H^+, 56776-18-2; **3a**,H^+, 91631-87-7; **3b**,H^+, 91631-88-8.

Methanol Attack on Highly Electrophilic 4,6-Dinitrobenzofurazan and 4,6-Dinitrobenzofuroxan Derivatives. A Kinetic Study

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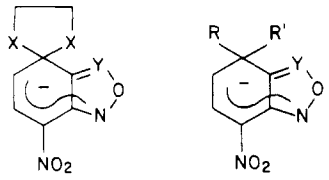
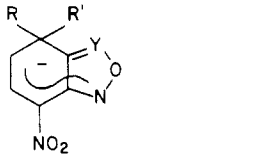
Methanol readily adds to the unsubstituted 7-carbons of 4,6-dinitrobenzofurazan (DNBZ) and 4,6-dinitrobenzofuroxan (DNBF) as well as the methoxy-bearing carbon of 7-methoxy-4,6-dinitrobenzofurazan (MDNBZ) to form the most stable methoxyl σ adducts known in this solvent. The formation and decomposition of the adducts are subject to general base and general acid catalysis, respectively, with β (α) values of ~0.50, indicating a concerted mechanism. The results suggest that methoxide ion behaves as a base catalyst for methanol addition rather than as a nucleophile. The intrinsic rate constants k_0 (in the Marcus sense) have been determined for the derivatives. Although the equilibrium constant for methanol addition to MDNBZ is somewhat greater than for addition to DNBZ and DNBF, the k_0 value for the latter derivatives is about 10-fold higher than that for MDNBZ. This indicates a higher intrinsic barrier for attack at a methoxy-bearing than at an unsubstituted carbon, in qualitative agreement with previously reported patterns in the benzene series. The high reactivity of DNBZ, DNBF, and MDNBZ toward methanol and other bases, together with the very high stability of the resulting adducts, emphasizes the superelectrophilic character of these electron-deficient aromatics.

There is now convincing evidence that mononitro-2,1,3-benzoxadiazoles and related *N*-oxides, currently known as nitrobenzofurazans and nitrobenzofuroxans, easily react with oxygen, sulfur, and nitrogen nucleophiles to form anionic σ complexes.[2-7] Complexes such as **1** and **2** have been fully characterized and isolated as crystalline



1, X = O, S; Y = N, N→O



2, R = R' = OMe; R = H, R' = OMe; Y = N, N→O

alkali salts.[3,5,6] Such characterization is of importance with respect to the proposal that the antileukemic properties exhibited by some of these derivatives may be related to their ability to form σ complexes with essential cellular SH and/or amino groups.[7]

Kinetic and thermodynamic studies have shown that the electrophilic character of 4-nitrobenzofurazans and benzofuroxans is comparable to that of 1,3,5-trinitrobenzene (TNB).[2,5,6] Since the introduction of a second nitro group must increase this character, the study of dinitro derivatives like 4,6-dinitrobenzofurazan (DNBZ) and 4,6-dinitrobenzofuroxan (DNBF) is of interest. Indeed, the latter compound, which is readily prepared by direct nitration of benzofuroxan[8] is known to behave as a super electrophile and can be used to assess the reactivity of very weak nucleophiles, including potential carbon nucleophiles like enols, anilines, or π-excessive heterocycles.[6,9-12] Also of interest is that the alkali salts of the formed adducts exhibit very strong explosive properties.[9a,11]

In view of these results, it was surprising to find no report regarding the furazan analogue of DNBF, i.e. DNBZ, in the literature. We have therefore undertaken efforts to synthesize this compound and compare its reactivity toward methanol and methoxide ion with that of DNBF. Following a preliminary communication of the p*K*a values in a recent review,[6] we now report detailed

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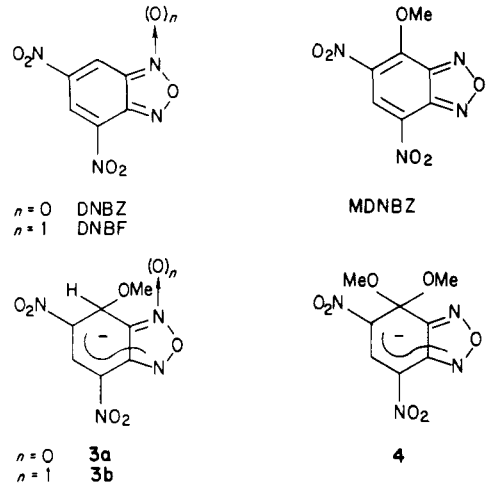
kinetic and thermodynamic results for the corresponding reactions which give the stable methoxy adducts **3a** and **3b**. For the purpose of comparison, we also report rate and equilibrium data for the formation of the *gem*-dimethoxy adduct **4** of 7-methoxy-4,6-dinitrobenzofurazan (MDNBZ).



While our work was in progress or essentially achieved,[6] two reports have appeared which describe the synthesis of DNBZ via direct nitration of 5-nitrobenzofurazan and reduction of the *N*-oxide group of DNBF, respectively.[13,14] Since it is the latter approach proposed by Read et al.[14] that we have also used, we will not reiterate here a discussion of the preparation of DNBZ. We will just mention that our experimental conditions (see Experimental Section) have provided this product in 65% yield, as compared with a 25% yield reported in ref 14.

Results

DNBZ (λ_{max} 310 nm), DNBF (λ_{max} 375 nm), and MDNBZ (λ_{max} 375 nm) behave similarly in methanol and give rapidly the very stable yellow-colored adducts **3a**, **3b**, and **4** in the absence of any added methoxide: λ_{max}^{3a} 465 nm; ϵ 27 300 M^{-1} cm^{-1}; λ_{max}^{3b} 460 nm; ϵ 29 170 M^{-1} cm^{-1}; λ_{max}^{4} 450 nm; ϵ 27 500 M^{-1} cm^{-1}. The three adducts have been characterized by their NMR spectra.[11b,14] An X-ray study of **4** has also been reported.[15]

Using the stopped-flow method, we were able to follow spectrophotometrically the kinetics of formation and/or decomposition of **3a**, **3b**, and **4** in the pH range 1.5–15 at 20 °C in methanol. In all cases, the appearance or disappearance of the adducts ($\sim 5 \times 10^{-5}$ M) was a clear first-order process. Dilute benzene sulfonic acid solutions, various buffer solutions, and dilute potassium methoxide solutions were used. The buffer solutions were prepared from either carboxylic acids or phenols (AH) and made up so as to give a total ionic strength of 0.02 M from the buffer species (A^-) alone without any added neutral salt.[16,17] The ionic strength of the dilute acid and base solutions was similarly maintained at 0.02 M by adding potassium bromide as needed. As shown previously, such a low ionic strength allows the mean activity coefficient $\gamma\pm$ to be calculated by using a simplified Debye-Hückel type equation: $\log \gamma\pm = -Bz^2\sqrt{I}$ with $B = 1{,}8$ at 20 °C in methanol.[16,17] This in turn allows the hydrogen ion concentration $[H^+]$ of the methanolic solutions to be deduced from the measured activity a_{H^+} of the solvated proton: $[H^+] = a_{H^+}/\gamma\pm$. The pH values are relative to the standard state in methanol.

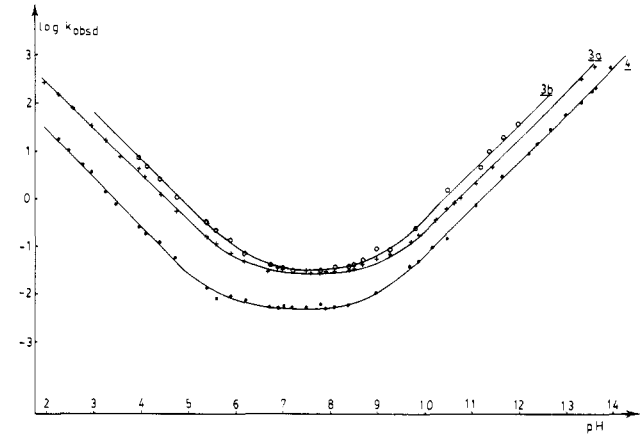


Figure 1. The pH dependence of k_{obsd} (s^{-1}) for the formation and decomposition of the adducts **3a**, **3b**, and **4** in methanol; 20 °C, I = 0.02 M.

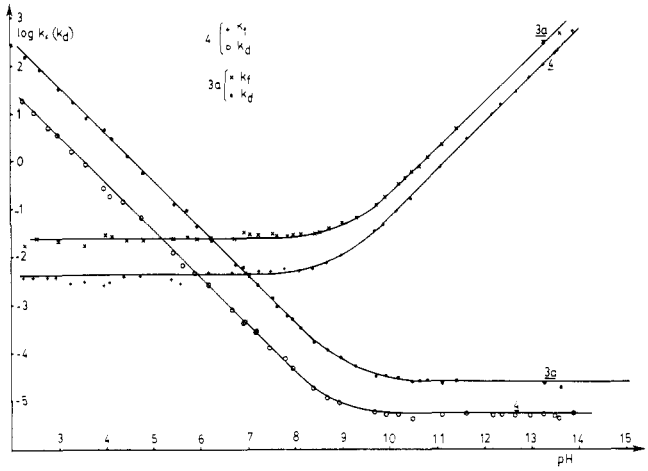


Figure 2. The pH dependence of k_f (s^{-1}) and k_d (s^{-1}) for the formation and decomposition of the adducts **3a** and **4** in methanol; 20 °C, I = 0.02 M.

The pH dependences of the observed first-order rate constants k_{obsd} for the combined formation and decomposition of **3a**, **3b**, and **4** are shown in Figure 1. Although our experimental conditions preclude the use of high buffer concentrations, appreciable buffer catalysis was observed in most cases. The k_{obsd} values used in Figure 1 and summarized in Table S_1[18] are therefore those extrapolated to zero buffer concentration. As can be seen, smooth pH–rate profiles are obtained despite the fact that buffers of varying chemical types were used.

Figure 2 shows the pH–rate profiles of the individual pseudo-first-order rate constants k_f and k_d for the formation and decomposition, respectively, of **3a** and **4**. These constants were calculated according to a previously described analysis,[6,17,19,20] using k_{obsd} values and the $pH_{1/2}$ (=

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Table I. Rate and Equilibrium Constants for Formation and Decomposition of the Adducts 3a, 3b, and 4 in Methanol; t = 20 °C, I = 0.02 M

	3a	3b	4
k_1^{MeOH}, s^{-1}	0.028	0.03	4.46×10^{-3}
$k_{-1}^{H^+}$, M^{-1} s^{-1}	2.09×10^4	4.68×10^4	1780
pK_a	6.05,[a] 6.12[b]	6.46,[a] 6.44[b]	5.93,[a] 5.85[b]
$k_2^{MeO^-}$, M^{-1} s^{-1}	9.30×10^5	1.87×10^6	2.52×10^5
k_{-2}, s^{-1}	2×10^{-5}	8.9×10^{-5}	4.9×10^{-6}
K_2, M^{-1} [c]	4.65×10^{10}	2.1×10^{10}	5.14×10^{10}

[a] Spectrophotometric determination. [b] From the intersection between the k_1^{MeOH} plateaus and the lines of slope −1 in Figures 2 and S_1. [c] $K_2 = k_2^{MeO^-}/k_{-2}$.

pKa[C] at I = 0.02 M) values corresponding to the half-formation of **3a** and **4** which were spectrophotometrically determined. These pH–rate profiles, as well as those for **3b** (Figure S1),[18] are consistent with Scheme I and eq 3–5.

Scheme I

$$S + CH_3OH \underset{k_{-1}^{H^+}}{\overset{k_1^{MeOH}}{\rightleftharpoons}} C + H^+ \quad (1)$$

$$S + CH_3O^- \underset{k_{-2}}{\overset{k_2^{MeO^-}}{\rightleftharpoons}} C \quad (2)$$

S = DNBZ, DNBF, MDNBZ C = **3a**, **3b**, **4**

$$k_f = k_1^{MeOH} + k_2^{MeO^-}[MeO^-] = k_1^{MeOH} + \frac{k_2^{MeO^-}K_s}{a_{H^+}\gamma\pm} \quad (3)$$

$$k_d = k_{-1}^{H^+}[H^+] + k_{-2} = \frac{k_{-1}^{H^+}a_{H^+}}{\gamma\pm} + k_{-2} \quad (4)$$

$$k_{obsd} = k_f + k_d \quad (5)$$

Complex formation may involve either methoxide ion ($k_2^{MeO^-}$) or methanol (k_1^{MeOH}) while the decomposition may occur spontaneously (k_{-2}) or via an H^+-catalyzed pathway ($k_{-1}^{H^+}$). The various rate coefficients were easily determined from the two linear portions of each of the k_f and k_d pH–rate profiles, using pKs = 16.86[16] in eq 3. They are summarized in Table I. It is also to be noted that the intersections in Figures 2 and S_1[18] between the k_1^{MeOH} plateaus and the corresponding straight lines of slope −1 yield the pK_a^C values for complex formation at I = 0.02 M. These are in good agreement with the pKa values thermodynamically determined.

As mentioned previously, appreciable buffer catalysis of the reactions has been observed, which was investigated in some detail for the three systems. In the most acidic buffers (trichloroacetic acid, dichloroacetic acid), only catalysis by the acid component (AH) was found to be operative in media of pH <5. Then, k_{obsd} is given by eq 6, because not only the $k^{A^-}[A^-]$ and $k_2^{MeO^-}[MeO^-]$ terms

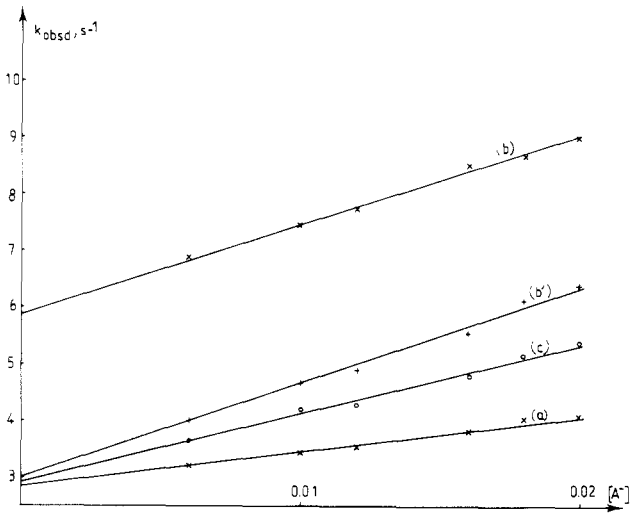


Figure 3. Variation of k_{obsd} with pH and concentration of the basic form A^- of the buffers: (a) DNBZ, 2,6-dichlorophenoxide buffer (pH = 11.11); (b) DNBF, 2,6-dichlorophenoxide buffer (pH = 11.11); (b') DNBF, 2,6-dichlorophenoxide buffer (pH = 10.81); (c) MDNBZ, *p*-cyanophenoxide buffer (pH = 11.65).

$$k_{obsd} = k_1^{MeOH} + k_{-1}^{H^+}[H^+] + k^{AH}[AH] \quad (6)$$

$$k_{obsd} = k_1^{MeOH} + k_2^{MeO^-}[MeO^-] + k^{A^-}[A^-] \quad (7)$$

but also the k_{-2} term are negligible. In reverse, only catalysis by A^- was observed in buffer solutions made up with 3,5-dinitrobenzoic acid, salicylic acid, *m*-chlorobenzoic acid, benzoic acid, 2,4,6-trichlorophenol, 2,6-dichlorophenol, and 4-cyanophenol (pH >6.7). In these instances, k_{obsd} is given by eq 7, i.e., the $k_{-1}^{H^+}[H^+]$, $k^{AH}[AH]$, and k_{-2} terms are negligible. Four representative buffer plots are shown in Figure 3. Working the data in terms of either eq 6 or eq 7 leads to the k^{AH} and k^{A^-} values summarized in Table II.

Discussion

General Features. Comparison of Figures 1 and 2 reveals that the k_{obsd} values measured for the three systems in the intermediate pH range 6–9 are close or identical with the corresponding k_f values. This shows that the formation of the adducts **3a**, **3b**, and **4** arises essentially from the attack of a methanol molecule on the parent substrates in this pH range.[6,17,19,20] It is only at pH ≥ about 9 that the attack of methoxide ion begins to compete with that of methanol, this pathway becoming predominant at pH >11.

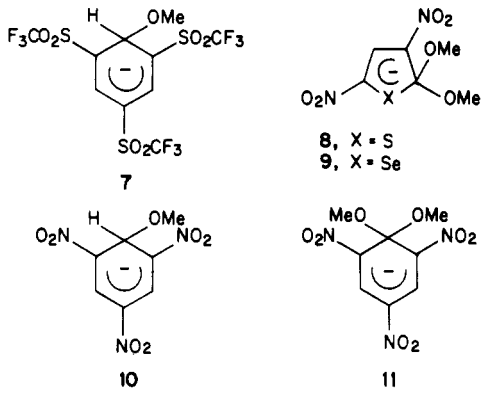
In view of the known reactivity of DNBF toward a number of weak nucleophiles, including water,[6,9,12,20] the

Table II. Rate Constants for Catalysis by Buffer Species[a]

		3a		3b		4	
buffer (basic species)	pK_a[b]	k^{AH}, M^{-1} s^{-1}	k^{A^-}, M^{-1} s^{-1}	k^{AH}, M^{-1} s^{-1}	k^{A^-}, M^{-1} s^{-1}	k^{AH}, M^{-1} s^{-1}	k^{A^-}, M^{-1} s^{-1}
methanol	−1.4	2.09×10^4[c]	1.13×10^{-3}[d]	4.68×10^4[c]	1.21×10^{-3}[d]	1780[c]	1.80×10^{-4}[d]
trichloroacetate	4.40	12		26		1.70	
dichloroacetate	5.89	1.1		2.95		0.15	
3,5-dinitrobenzoate	6.71		1, 7				
salicylate	7.50		1		1.3		0.10
m-chlorobenzoate	8.41			0.18[f]	16		
benzoate	8.97	0.024[f]	20	0.077[f]	25	3.63×10^{-3}[f]	4
2,4,6-trichlorophenoxide	10.18		20		59		4.5
2,6-dichlorophenoxide	11.11		60		158		22
p-cyanophenoxide	11.72	1.07×10^{-3}[f]	500	3.80×10^{-3}[f]	700	1.95×10^{-4}[f]	120
methoxide ion	18.26	8.1×10^{-7}[g]	9.30×10^5[e]	3.60×10^{-6}[g]	1.87×10^6[e]	1.98×10^{-7}[g]	2.52×10^5[e]

[a] I = 0.02 M, t = 20 °C. [b] pK_a at I = 0.02 M. [c] $k^{AH} = k_{-1}^{H^+}$. [d] Obtained from $k_1^{MeOH}/24.7$. [e] $k^{A^-} = k_2^{MeO^-}$. [f] Calculated from $k^{AH} = k^{A^-}K_a^{AH}/K_a^C$. [g] Calculated from $k_{-2}^{exp}/24.7$.

ease of reaction of methanol with this compound as well as with DNBZ and MDNBZ is perhaps not unexpected. The kinetic and thermodynamic data of Table I are of interest, however, because their comparison with data previously reported for the formation of other methoxy complexes in methanol provides a quantitative illustration of the reactivity of these derivatives. The latter is well demonstrated both by the efficiency of the methanol pathway of the formation of **3a**, **3b**, and **4** and the very high thermodynamic stability of these adducts; pKa^{3a} = 6.05; pKa^{3b} = 6.46; pKa^{4} = 5.93. In fact, examples of complex formation where methanol attack is the predominant pathway have not been observed previously.[6] Thus, such a process was found to contribute only for about 10–15% to the formation of the complex **7**, i.e., the most stable benzene σ complex known, despite the finding of a k_1^{MeOH} value (3.02×10^{-2} s^{-1}) similar to those found for the DNBF (0.03 s^{-1}) and DNBZ (0.028 s^{-1}) systems. In this instance, the importance of the solvent pathway appears to be considerably reduced by the much higher susceptibility of **7** ($k_{-1}^{H^+} = 2.88 \times 10^7$ L mol^{-1} s^{-1}; k_{-2} = 0.011 s^{-1}) than of **3a** ($k_{-1}^{H^+} = 2.09 \times 10^4$ L mol^{-1} s^{-1}; $k_{-2} = 2 \times 10^{-5}$ s^{-1}) and **3b** ($k_{-1}^{H^+} = 4.68 \times 10^4$ L mol^{-1} s^{-1}; $k_{-2} = 8.9 \times 10^{-5}$ s^{-1}) to the H^+-catalyzed and uncatalyzed decompositions. The result is a 10^3-fold lower thermodynamic stability of **7** (pKa^{MeOH} = 9.12 at 20 °C) and the existence of a very



narrow pH range, i.e., 9–10, where the contribution of the methanol attack (k_1^{MeOH}) to the observed rate of formation of **7** is not completely overshadowed by either the k_{-2} and $k_{-1}^{H^+}[H^+]$ terms associated with the decomposition pathways (pH <9) or the $k_2^{MeO^-}[MeO^-]$ term associated with the formation of **7** ($k_2^{MeO^-} = 3.9 \times 10^5$ L mol^{-1} s^{-1}) from methoxide ion attack (pH >10). On the other hand, methanol attack could be detected only to a small extent (2–3%) in the formation of the heterocyclic complexes **8** and **9** (pKa^8 = 11.36 and pKa^9 = 10.07 at 20 °C)[17a] but did not occur at all in that of the trinitrobenzene complexes **10** and **11** (pKa^{10} = 15.51, pKa^{11} = 11.57 at 20 °C),[21] which serve as the usual references for assessing the stability of methoxyl and *gem*-dimethoxyl adducts in benzene series.[6] These observations emphasize the super electrophilic character of the dinitrobenzofurazan and benzofuroxan derivatives, which is the consequence of the strong electron-withdrawing effect of both the nitro groups and the annelated furazan or furoxan ring as well as the relatively low aromaticity of the benzofurazan and benzofuroxan systems.[6,22]

Buffer Catalysis. The Brønsted plots for acid–base catalysis of the formation and decomposition of the

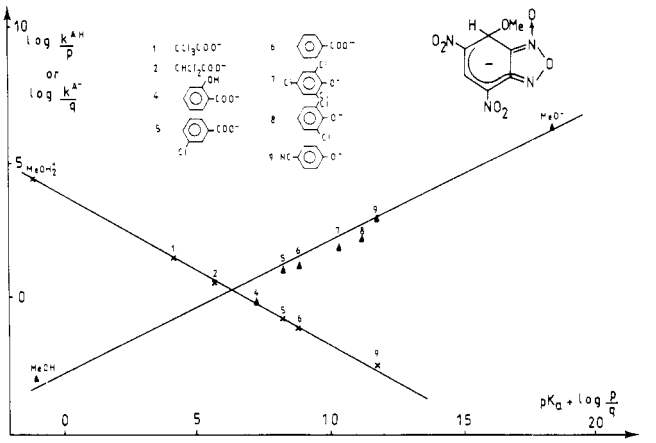


Figure 4. Brønsted plots for the formation and decomposition of the adduct **3b** in methanol; 20 °C, I = 0.02 M; k^{AH} and k^{A^-} in M^{-1} s^{-1}.

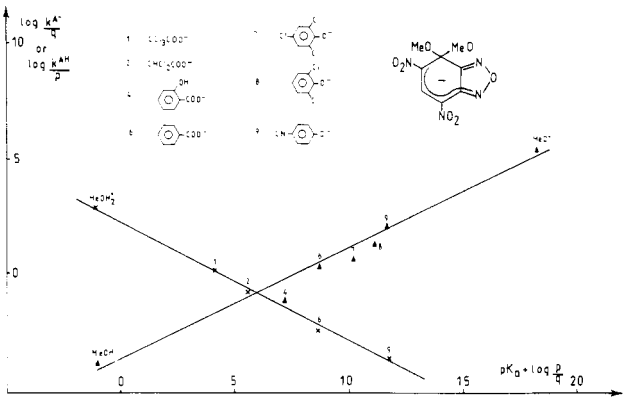
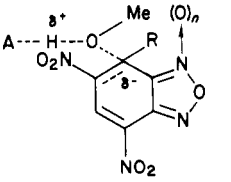


Figure 5. Brønsted plots for the formation and decomposition of the adduct **4** in methanol; 20 °C, I = 0.02 M; k^{AH} and k^{A^-} in M^{-1} s^{-1}.

methoxy benzofuroxan adduct **3b** and the dimethoxy benzofurazan adduct **4** are shown in Figures 4 and 5, respectively. As can be seen, the rate constants k^{A^-} for 3-chlorobenzoate, benzoate and *p*-cyanophenoxide ion catalysis, together with those for MeO^- and methanol attack (k_1^{MeOH}/24.7) define reasonable Brønsted lines of slopes 0.50 and 0.48, respectively. A similar correlation (shown in Figure S2) is obtained for the methoxybenzofurazan adduct **3a** with β = 0.49. Such β values are of the same order as those recently reported for the hydrolysis of a number of aromatic electrophiles, e.g., picryl chloride, picrylimidazole, and 3-methyl-1-picrylimidazolium cation,[23,24] for water attack on DNBF to give the hydroxyl analogue of **3b**[20] as well as for many other hydration reactions of electrophilic carbon centers.[25,26] This favors a concerted mechanism with a transition state like **12**.[27,28]



12, R = H, OMe; n = 0, 1

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Table III. Experimental Brönsted β and α Values and Intrinsic Rate Constants

	DNBZ	DNBF[a]	MDNBZ
β	0.49	0.50	0.48
α	0.54	0.55	0.50
log k_0	0	0.20	−0.80

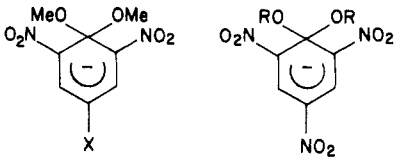
[a] β = 0.45 in aqueous solution.[20]

The fact that the point for salicylate ion catalysis exhibits an appreciable negative deviation in the three systems presumably reflects the existence of hydrogen bonding in this catalyst.

The observation that the rate of catalysis by MeO^- lies on the same Brønsted line as k^{A^-} for the buffer bases is to be noted since it suggests that methoxide ion acts as a base catalyst for methanol addition rather than as a nucleophile.[20,23,30] Although it is unexpected on the basis of the libido rule formulated by Jencks for OH^-[31] but also applicable on ground of analogy to MeO^-, this behavior is consistent with similar findings in the hydroxide addition to a number of aromatic or olefinic electrophiles[19,23,30c] and some carbocations.[32] Why catalysis of methanol addition may be a more favorable process than direct nucleophilic attack is certainly understandable in the same terms as those first discussed by Ritchie for OH^- in aqueous solution.[30]

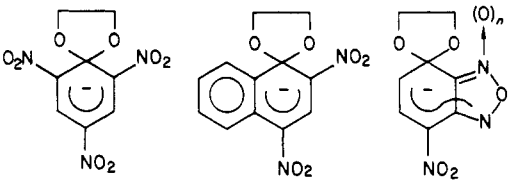
As required on the basis of microscopic reversibility, the decomposition of **3a**, **3b**, and **4** is subject to general acid catalysis. In the three systems, the k^{H^+} value and the k^{AH} values for trichloracetic and dichloracetic acids provide satisfactory Brønsted lines with slopes close to 0.5 (Table III). The k^{AH} values for *p*-cyanophenol, benzoic acid, and 3-chlorobenzoic acid calculated from the relation $k^{AH} = k^{A^-} Ka^{AH}/Ka^C$[33] also lie on these lines which confirm a transition state like **12**. Interestingly, concerted acid-catalyzed decomposition of a number of *gem*-dialkoxy adducts, e.g., **13** and **14**, and spiro adducts, e.g., **15**, **16**, and **17**, was previously observed.[5b,34,35]

Intrinsic Rate Constants. Of particular interest is that the systems under study represent the first examples of σ complex reactions where both the acid–base-catalyzed pathways could be simultaneously observed. For each system, the Brønsted plots for acid and base catalysis intersect at a point where $pKa^{AH} + \log p/q \simeq pKa^{adduct}$, as expected. This allows the determination of the absolute intrinsic rate constants k_0 for the three substrates.[36-38]



13 14

X = SO_2CF_3, NO_2, CN, SO_2Me, CF_3; R = Me, Et, $CH_3OCH_2CH_2$, $ClCH_2CH_2$, $HC{\equiv}C{-}CH_2$



15 16 17, n = 0, 1

These parameters, which are given in Table III, permit us to draw the following conclusions:

(1) The intrinsic reactivity of DNBZ and DNBF, which both add a methoxy group at an unsubstituted carbon, is very similar, pointing out that the annelated furazan and furoxan moities exert a very comparable activating effect on the complexation process. This confirms previous observations made in methoxide ion addition to the 4-mononitro derivatives.[5b,39]

(2) The intrinsic reactivity of MDNBZ, which adds a methoxy group to a methoxyl bearing carbon, is about 10-fold lower than that of DNBZ and DNBF. In contrast, the resulting *gem*-dimethoxyl adduct **4** is slightly more stable than the monomethoxyl analogues **3a** and **3b**; $pKa^4 - pKa^{3a} = 0.12$; $pKa^4 - pKa^{3b} = 0.53$. While these observations are consistent with general reactivity patterns found for formation of monomethoxy and *gem*-dimethoxy complexes,[6] the observed differences in reactivity and stability of **3a** (**3b**) and **4** are not as large as those found in the benzene series between complexes like the TNB and TNA adducts **10** and **11**; $pKa^{10} - pKa^{11} \simeq 4$; $k_2^{MeO^-}(11)/k_2^{MeO^-}(10) = 2.3 \times 10^{-3}$ at 20 °C.[21] In this latter case, steric effects associated with the TNA system, namely steric hindrance to the approach of the reactant (F-strain) and relief of steric strain on formation of **11**, are the predominant factors determining the relative reactivities and stabilities of **10** and **11**.[6] In contrast, it is presumably the much lower aromaticity and the considerable electron-deficient character of the dinitrobenzofurazan and dinitrobenzofuroxan substrates which are the predominant factors governing the relative reactivities and stabilities of **3a**, **3b**, and **4** (vide supra). The result is that steric effects, even though they are present to some extent in the MDNBZ system, do not appear to play a significant role in the formation of these adducts.

Experimental Section

Materials. 4,6-Dinitrobenzofuroxan was prepared by the procedure of Drost,[8] mp 173 °C (lit.[8,11b] mp 172–174.5 °C). 4,6-Dinitro-7-methoxybenzofurazan was prepared from simple nitration of 4-methoxy-7-nitrobenzofurazan, mp 151 °C (lit.[11b,40] mp 149–151 °C).

4,6-Dinitrobenzofurazan was prepared according to the following method. Triphenylphosphine (6 g) was dissolved in the minimum amount of xylene. The resulting solution was added

(28) It is perhaps to be noted that phenoxide ions do not simply behave as general base catalysts for the formation of **3a**, **3b**, and **4** when the reactions are carried out in methanolic solutions rich in Me_2SO (>50%) instead of methanol. In these instances, the methoxy adducts **3a**, **3b**, and **4** remain the final products formed in the phenoxide buffer solutions but their appearance is preceded by the very fast formation of short-lived species with visible spectra close but not identical with those of **3a**, **3b**, and **4**. These are presumably the corresponding aryloxy adducts which arise from direct nucleophilic attack of the phenoxide ions on DNBZ, DNBF, and MDNBZ. In agreement with literature data,[29] these adducts are thermodynamically much less stable than their methoxy analogues and undergo a complete conversion into **3a**, **3b**, and **4**. These reactions are currently under investigation in the laboratory.

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dropwise with agitation and under argon atmosphere to a solution of DNBF in xylene (5 g, 250 cm^3) which was previously warmed to 80 °C on an oil bath. After the addition, the solution was heated to about 110 °C for 1 h, then maintained at 100 °C for a further 5 h, and cooled. The solvent was removed under reduced pressure, yielding a dark residue which was purified by column (40 cm long, 5 cm diameter) chromatography, using Florisil as the adsorbent and benzene–hexane mixtures as the eluent. Employment first a 75:25 (v/v) hexane–benzene mixture allowed the unreacted DNBF to be eluted. Then, the benzene content of the elution mixture was increased progressively from 25% to 50% to 75%. Concentration of the corresponding filtrates yields orange crystals of DNBZ (3.06 g, 65.8%). The melting point was obtained after recrystallization from carbon tetrachloride, mp 133 °C (lit.[13,14] 129–132 °C). Note that heating the xylene solutions at reflux results in a decrease in the yields of DNBZ.

The other materials were reagent grade and were used without further purification.

Rate and pH Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer the cell compartment of which was maintained at ±0.5 °C. 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% with the exception of some k^{A^-} and k^{AH} rate constants which may be to ±10% in some cases.

The pH of the buffer solutions was measured on a Radiometer Model pH meter according to standard methods.[16] The pH values are relative to the standard state in pure methanol.[16,17]

Registry No. 3a, 91948-44-6; **3b**, 91948-45-7; **4**, 61487-11-4; DNBZ, 70264-71-0; DNBF, 5128-28-9; MDNBZ, 22714-04-1.

Supplementary Material Available: Observed first-order rate constants k_{obsd} for the formation and/or decomposition of the adducts **3a**, **3b**, and **4** in methanol (Table S1), the pH dependence of k_f (s^{-1}) and k_d (s^{-1}) for the formation and decomposition of the adduct **3b** in methanol at t = 20 °C, I = 0.02 M (Figure S1), and the Brønsted plots for the formation and decomposition of the adduct **3a** in methanol at t = 20 °C and I = 0.02 M (Figure S2) (3 pages). Ordering information is given on any current masthead page.

The Effect of Lewis Acid and Solvent on Concerted 1,2-Acyl Migration

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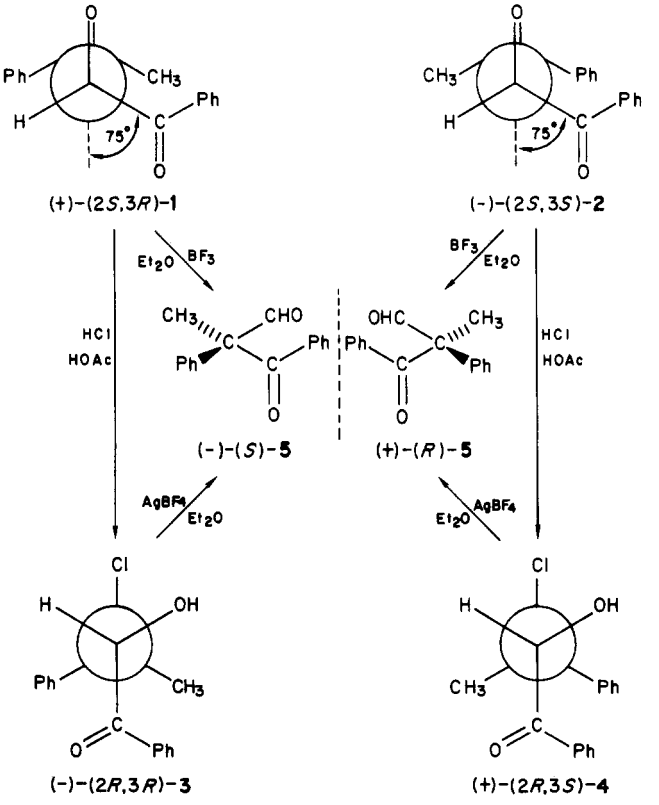
Lewis acid catalyzed 1,2-benzoyl migration in (*E*)- and (*Z*)-1,3-diphenyl-2-buten-1-one oxides (dypnone oxides) is a concerted process that occurs with inversion of configuration at the migration terminus when nonpolar solvents are employed. In methanol solvent acid-catalyzed epoxide ring opening occurs with net retention of configuration affording a mixture of diastereomers of 1,3-diphenyl-2-hydroxy-3-methoxy-1-butanone and with no detectable acyl migration. A mechanism is postulated for carbonyl migration that involves reverse polarization of the carbonyl π-bond. The concerted 1,2-acyl migration is suggested to involve neighboring group participation at carbonyl carbon in the rate limiting step.

The unusual migratory propensity of the carbonyl group was first established by House in a series of mechanistic papers.[2] Carbonyl migration, catalyzed by boron trifluoride, has been reported with epoxy ketones,[2] esters,[3] and thiol esters.[4] This intramolecular migration[2c] has also been used in several synthetic applications.[5] Our efforts have been directed toward establishing the concerted nature of this reaction. We have shown that 1,2-carbethoxy migration in ethyl (*E*)-3-methyl-3-phenylglycidate occurred with inversion of configuration and without loss of optical purity.[6a] We have also excluded a carbenium ion intermediate in the rearrangement of (*E*)- and (*Z*)-1,3-diphenyl-2-buten-1-one oxides (dypnone oxides, **1** and **2**).[6b] The silver ion catalyzed carbonyl migration with chiral chlorohydrins **3** and **4** also proceeded with complete in-

Scheme I



(1) National Science Foundation Predoctoral Fellow.

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