The above initial procedure was again repeated and *n*-butyllithium (0.33 mL, 1.6 M, pentane) was used as the alkylating agent. Again, no evidence of a dihydroanthracene was detected.

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Supplementary Material Available: ^1H NMR spectra for compounds **7**, **9**, **10**, **11**, and **14**, ^{13}C NMR spectra for compounds **7**, **9**, **10**, and **11**, and mass spectra for compounds **7**, **9**, **10**, and **14** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

4,6-Dinitro-7-methylbenzofuroxan: A Strong Carbon Acid of Very Low Intrinsic Reactivity

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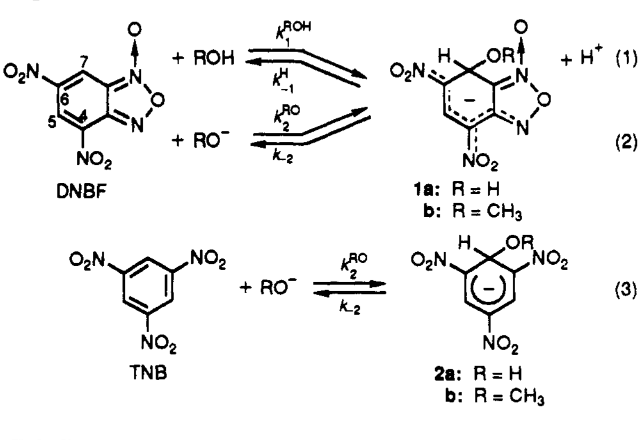
Rates of ionization of 4,6-dinitro-7-methylbenzofuroxan (**3**) by water, hydroxide ion, and various general bases have been measured in aqueous solution at $t = 25$ °C. The solvent pathway is the major process contributing to the formation of the resulting carbanion (C-3) in solutions of pH ≤ 8. The very high thermodynamic stability of C-3 ($pK_a^{CH} = 2.50$), the exocyclic carbon of which is essentially olefinic in nature, is shown to derive for the most part from an extensive delocalization of the negative charge through the two nitro groups and the annelated furoxan ring. In agreement with the idea that considerable molecular, electronic, and solvational reorganization is required to produce a highly delocalized carbanion, the deprotonation of **3** is associated with one of the highest intrinsic energy barriers for proton transfer so far measured in aqueous solution ($\Delta G_0^{\ddagger} = 85.5$ kJ mol^{-1}). The strong acidity of **3** also emphasizes the exceptional activating effect of a 4,6-dinitrobenzofuroxan moiety.

There is much evidence that dinitrobenzofuroxan derivatives are extremely electron-deficient and therefore very "acidic" heteroaromatics.[1-10] The high tendency of 4,6-dinitrobenzofuroxan (DNBF) to undergo σ-complexation in the absence of any added base in aqueous or methanolic solution is illustrative for this behavior.[3,4] The pK_a's for the formation of the hydroxy and methoxy adducts **1a** and **1b** according to eq 1 are equal to 3.75 ($t = 25$ °C) and 6.45 ($t = 20$ °C), respectively, in the corresponding solvents. This makes these σ-complexes about 10^{10} times more stable than the analogous adducts **2a** and **2b** of 1,3,5-trinitrobenzene, which are the common references in σ-complex chemistry.[3,4] Use of alkali hydroxide or methoxide solutions is in fact necessary to achieve the formation of **2a** and **2b** in water and methanol, respectively (eq 3).[11]



DNBF

1a: R = H
b: R = CH$_3$

TNB

2a: R = H
b: R = CH$_3$

Two main factors are believed to contribute to the exceptional ease of formation and stability of **1a** and **1b**.[1,2] The first is the relatively low aromaticity of the benzofuroxan system which is expected to favor the covalent addition compared to most aromatic and heteroaromatic systems. The second factor is the combination of the strong electron-withdrawing effects of the two nitro groups and the annelated furoxan ring. The result is not only a high electron-deficiency at C-7 of DNBF, and hence a high susceptibility of this ring position to nucleophilic attack, but also a high electron-delocalizing capability of the negative charge which enhances the stability of the resulting σ-adducts.

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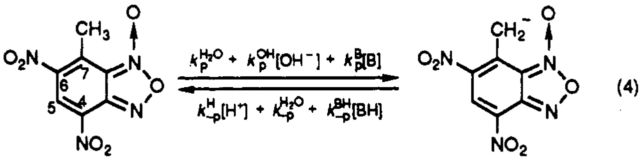
Recently, it has become clear that there is a close relationship between the intrinsic barriers associated with the ionization of carbon acids and the degree of resonance stabilization of the resulting carbanions.[12-19] In this respect, the exceptional ability of a DNBF moiety to stabilize σ-adducts like **1a** and **1b** suggested that a carbon acid which would be activated by this structure might exhibit a very low intrinsic reactivity. This idea led us to investigate the kinetics and thermodynamics of the ionization of 4,6-dinitro-7-methylbenzofuroxan (**3**) by various bases (eq 4) in aqueous solution. We now report the details of this work.



(4)

3 C-3

Results

At low concentrations ($\approx 3 \times 10^{-5}$ M), in aqueous solution, 4,6-dinitro-7-methylbenzofuroxan (**3**, λ_{max} = 415 nm, ϵ = 6850 L mol^{-1} cm^{-1}) undergoes a rather slow ($t_{1/2} \approx 10$ min) but essentially complete conversion to the red-colored carbanion C-3 (λ_{max} = 480 nm, ϵ = 12 800 L mol^{-1} cm^{-1}) in the absence of any added base. The pK_a^{CH} value of **3** was determined from the observed variations in the optical density measured at 480 nm after completion of the equilibrium formation of C-3 in various dilute HCl solutions and various formic and acetic acid buffer solutions. A pK_a^{CH} value of 2.50 was thus obtained at 25 °C (I = 0.1 mol L^{-1} KCl).

Rates of deprotonation of **3** by water, hydroxide ion, and a variety of buffer bases (B) of $pK_a \geq 3.45$ and of protonation of C-3 by hydronium ion, water, and the conjugated buffer acids (BH) were measured either in a conventional or a stopped-flow spectrophotometer. The reactions can be described by the general equation (4), which assumes that **3** does not exist appreciably in the aci form **3'** (vide infra). The rates of proton transfer were measured at 25 °C and I = 0.1 M.

At pH $\leq pK_a^{CH}$ equilibrium 4 was approached from pH-jump experiments. These were carried out by mixing equal volumes of a solution of the carbanion C-3 ($\approx 3 \times 10^{-5}$ M) in an acetic acid buffer (pH = 4.64; [B$^-$] = [BH] = 0.005 M) and of a HCl solution (0.01–0.205 M) made up so as to attain the desired final pH. At pH $\geq pK_a^{CH}$, the equilibrium 4 was approached from left to right in two different ways. On the one hand, advantage has been taken of the slow "spontaneous" ionization of **3** to prepare fresh "neutral" solutions of this substrate ($\approx 3 \times 10^{-5}$ M) and mix them rapidly with the appropriate HCl (10^{-3}–(5×10^{-3}) M), buffer, or KOH ((1.3×10^{-3})–0.02 M) solutions. On the other hand, pH-jump experiments were carried out by mixing a 0.01 M HCl solution of **3** with the desired buffer or base reagents. The rate data obtained in the two series of experiments for a given final pH were identical within experimental error. To be noted is the observation of a rapid decomposition of C-3 in basic solutions. We are currently investigating further this decomposition which is apparently the result of a radicalar self-condensation of the carbanion to give the bis-DNBF derivative **4**.[20]

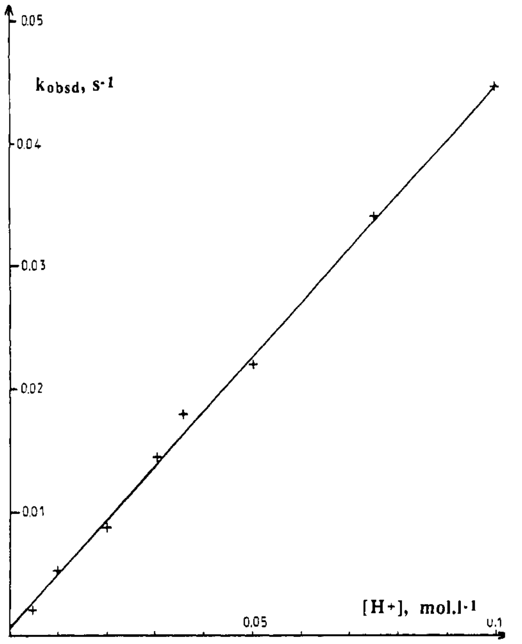
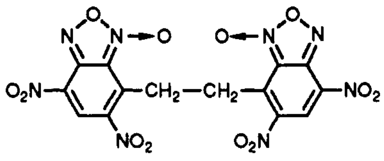


Figure 1. Effect of the hydronium ion concentration on the observed rate constant (k_{obsd}) for reaction 4 in aqueous solution; t = 25 °C, I = 0.1 M.



4

In all instances, the rates were determined under pseudo-first-order conditions with a large excess of the acid, base, or buffer reagent over the substrate concentration. Under these experimental conditions, the observed rate constant, k_{obsd} for approach to equilibrium 4, is given by eq 5:

$$k_{obsd} = k_p^{H_2O} + k_p^B[B] + k_p^{OH}[OH^-] + k_{-p}^H[H^+] + k_{-p}^{BH}[BH] + k_{-p}^{H_2O} \quad (5)$$

The evaluation of the various rate constants of eq 5 was made as follows. In dilute KOH solutions, eq 5 simplifies to eq 6 so that k_p^{OH} was simply obtained from the slope of a plot of k_{obsd} vs [OH$^-$] which was linear with a negligible intercept; k_p^{OH} = 1200 L mol^{-1} s^{-1}. Using the k_p^{OH} value, the rate constant $k_{-p}^{H_2O}$ was calculated from $k_{-p}^{H_2O} = k_p^{OH}K_w/K_a^{CH}$, where K_w is the autoprotolysis constant at I = 0.1 M (pK_w = 13.78 at T = 25 °C):[21] $k_{-p}^{H_2O} \approx 4 \times 10^{-9}$ s^{-1}. In HCl solutions, eq 5 reduces to eq 7. As a matter of fact, an

$$k_{obsd} = k_p^{OH}[OH^-] + k_{-p}^{H_2O} \quad (6)$$

$$k_{obsd} = k_{-p}^H[H^+] + k_p^{H_2O} \quad (7)$$

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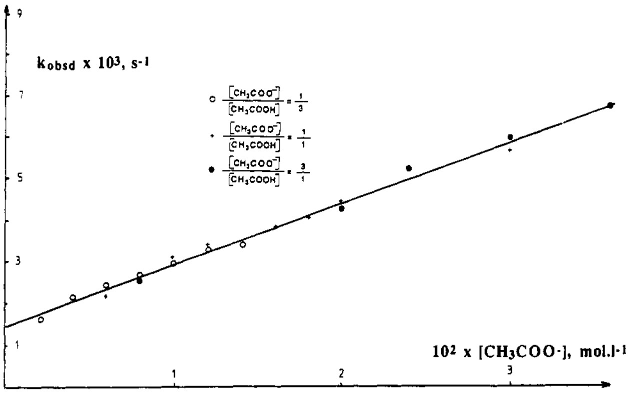

Figure 2. Effect of buffer concentration and pH on the observed rate constant (k_{obsd}) for reaction 4 in aqueous solution: $t = 25$ °C, $I = 0.1$ M.

excellent straight line was obtained on plotting k_{obsd} vs [H$^+$] (Figure 1). While the slope of this line readily afforded $k^{H}_{-p} = 0.43$ L mol^{-1} s^{-1}, the intercept was too uncertain to provide a reliable estimation of $k^{H_2O}_{p}$. This rate constant was therefore calculated as $k^{H_2O}_{p} = K^{CH}_{a} k^{H}_{-p} = 1.36 \times 10^{-3}$ s^{-1}. This value shows that $k^{H_2O}_{-p}$ is in fact negligible compared to $k^{H_2O}_{p}$.

The k^{BH}_{-p} and k^{B}_{p} values were obtained from kinetic experiments conducted at various buffer ratios with k_{obsd} being determined at six–eight different buffer concentrations at any given pH. Since appreciable catalysis was only found in buffers of p$K_a \geq 3.45$, the contributions of the k^{H}_{-p}[H$^+$] and k^{BH}_{-p}[BH] terms were essentially negligible in all cases. As illustrated in Figure 2, which refers to the experiments carried out in various acetic acid buffers, plots of k_{obsd} vs [B] for any given buffer of p$K_a < 7.5$ were linear with points determined at different pH falling on the same straight line. Results are therefore consistent with the simplified equation (8).

$$k_{obsd} = k^{H_2O}_{p} + k^{B}_{p}[B] \qquad (8)$$

The slopes of the k_{obsd} vs [B] plots afforded directly the k^{B}_{p} values for the different buffers studied while the intercepts were all equal to $k^{H_2O}_{p} = (1.4 \pm 0.1) \times 10^{-3}$ s^{-1} (Table S1), in good agreement with the $k^{H_2O}_{p}$ value previously determined in HCl solutions. With the TES (pK_a = 7.69) and CAPS (pK_a = 10.02) buffer solutions, the contribution of the hydroxide ion to the base catalysis was no longer negligible. In agreement with eq 9,

$$k_{obsd} = k^{H_2O}_{p} + k^{B}_{p}[B] + k^{OH}_{p}[OH^-] \qquad (9)$$

excellent and parallel linear plots of k_{obsd} vs [B] were obtained at the different pH's studied, thus allowing a facile determination of the corresponding k^{B}_{p} values. The intercepts of these plots had values consistent with the expected contribution of the k^{OH}_{p}[OH$^-$] term, as calculated from the value of k^{OH}_{p} measured in dilute hydroxide solutions. With the *p*-cyano- and *p*-chlorophenol buffers (pK_a = 7.89 and 9.38 respectively), linear plots of k_{obsd} vs [B] were also obtained but the catalysis of the deprotonation of **3** by the phenoxide ions was so efficient that the intercepts of these plots were too small to check accurately the contribution of the hydroxide ion catalysis.

The various rate parameters associated with the interconversion of **3** and C-3 according to eq 4 are summarized in Table I. All quoted k^{BH}_{-p} values were calculated by means of eq 10:

$$k^{BH}_{-p} = k^{B}_{p}\frac{K^{BH}_{a}}{K^{CH}_{a}} \qquad (10)$$

Table I. Rate Constants for Reactions 4 in Aqueous Solution[a]

	buffer acid	pK^{BH}_{a} [b]	k^{B}_{p}, L mol^{-1} s^{-1}	k^{BH}_{-p}, L mol^{-1} s^{-1}
1	H_3O^+	−1.74	$1.36 \times 10^{-3}/55.55$[c]	0.43
2	methoxyacetic acid	3.45	0.023	2.58×10^{-3}[d]
3	formic acid	3.60	0.035	2.78×10^{-3}[d]
4	acetic acid	4.64	0.12	8.7×10^{-4}[d]
5	succinate anion	5.60	0.41	3.27×10^{-4}[d]
6	cacodylic acid	6.15	0.74	1.65×10^{-4}[d]
7	$H_2PO_4^-$	6.70	1.24	7.82×10^{-5}[d]
8	TES[e]	7.69	2.90	1.87×10^{-5}[d]
9	4-cyanophenol	7.89	51	2.08×10^{-4}[d]
10	4-chlorophenol	9.38	500	6.59×10^{-5}[d]
11	CAPS[f]	10.33	93	1.37×10^{-6}[d]
12	H_2O	15.74	1200	$4 \times 10^{-9}/55.55$[g]

[a] $t = 25$ °C; $I = 0.1$ M KCl; experimental error in the measured rate constants k^{B}_{p} or k^{BH}_{-p}, ±5% or better; in pK^{BH}_{a} and pK^{CH}_{a}, ±0.05 pK unit; in calculated rate constants k^{B}_{p} or k^{BH}_{-p}, ±10%. [b] Potentiometrically measured pK^{BH}_{a} values at $I = 0.1$ M KCl. [c] $k^{H_2O}_{p}/55.55$ with $k^{H_2O}_{p}$ calculated from $K^{CH}_{a}k^{H}_{-p}$. [d] k^{BH}_{-p} calculated from eq 10. [e] TES = 2-[tris(hydroxymethyl)methylamino]-1-ethanesulfonic acid. [f] CAPS = 3-(cyclohexylamino)-1-propanesulfonic acid. [g] $k^{H_2O}_{-p}/55.55$ with $k^{H_2O}_{-p}$ calculated from $k^{OH}_{p}K_w/K^{CH}_{a}$; $K_w = 1.66 \times 10^{-14}$ at $I = 0.1$ M KCl.[21]

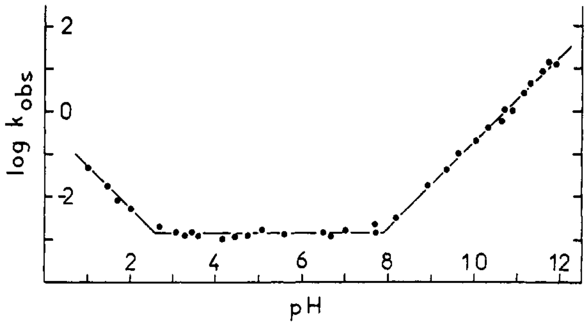

Figure 3. pH dependence of the observed rate constant for reaction 4 at zero buffer concentration in aqueous solution: $t = 25$ °C, $I = 0.1$ M.

Using the rate data of Table S1 which refer to the equilibrium approach at zero buffer concentration and different pH, the pH–rate profile for the ionization of **3** could be drawn and is given in Figure 3.

Discussion

Deprotonation of **3** by the solvent molecules appears to be the operative pathway leading to the carbanion C-3 not only in the absence of any added base but also in the presence of low to moderate concentrations of base catalysts of p$K_a \leq 7$. As evidenced by the pH–rate profile of Figure 3, it is only at pH > 8 that the deprotonation of **3** by hydroxide ion begins to offset significantly the water reaction. Such an important role of the solvent was not found in studying the ionization of the numerous nitro-activated carbon acids which have so far been investigated in aqueous solution.[17,22–27] Only in the presence of Me_2SO, a solvent which is known to strongly enhance the basicity of water molecules, was an appreciable contribution of the solvent to the ionization of some relatively strong carbon acids, e.g., 2,2′,4,4′,6,6′-hexanitrodiphenylmethane (pK_a =

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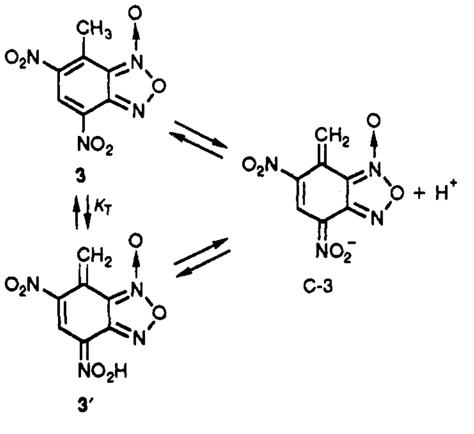
5.01 in 50:50 H_2O–Me_2SO), previously reported.[18]

The importance of the solvent pathway in reaction (4) is probably related to the very high thermodynamic acidity of **3** which is half-ionized in an hydrochloric acid solution, $\approx 3 \times 10^{-3}$ M. This result emphasizes the exceptional activating effect of the 4,6-dinitrobenzofuran moiety.[1-5] The acidity of **3** is 10^{11} times greater than that of 2,4,6-trinitrotoluene ($pK_a^{CH} = 13.60$ in water),[28] which is the common model for comparison of reactions involving benzylic-type carbon acids.[29,30,31] Preliminary measurements give a pK_a^{CH} value of 5.20 for the ionization of **3** in methanol, confirming the acidity difference quoted above between this compound and TNT ($pK_a^{CH} = 15.60$ in methanol)[28] and showing that the DNBF structure is also considerably more acidifying than a 2,4,6-tris[(trifluoromethyl)sulfonyl]phenyl moiety. The pK_a^{CH} value for the ionization of the corresponding toluene **5** in methanol is 9.46 at 25 °C.[32] On the other hand, the acidity of **3** is much greater than that of a number of carbon acids which benefit from the very efficient activation of a nitro group directly attached to the ionizable carbon atom, e.g., nitromethane ($pK_a^{H_2O} = 10.28$),[26] phenylnitromethane ($pK_a^{H_2O} = 6.77$),[26] 1,1-dinitroethane ($pK_a^{H_2O} = 5.24$),[22] or 1,1-dinitromethane ($pK_a^{H_2O} = 3.57$).[33] Only trinitromethane ($pK_a^{H_2O} = 0.14$)[34] has a greater acidity than does **3**.

Nitro-activated carbon acids of the strength of **3** often exist as a tautomeric mixture of nitro and aci forms.[35,36] In the case of **3**, our experiments show that the observed rate constant k_{obsd} for reprotonation of C-3 in hydrochloric acid solutions depends linearly on the H^+ concentration up to $[H^+] = 0.1$ M (Figure 1). This result indicates that protonation of C-3 on oxygen to form the aci form **3′** (or its *o*-nitro analogue) in a rapid preequilibrium is insignificant under our experimental conditions, implying that the $pK_a^{NO_2H}$ value of the aci form is <0.5 in aqueous solution and that the equilibrium constant K_T in eq 11 is <0.01. The assumption that the aci form **3′** would be more favored than its ortho–nitro analogue is based on the well-known feature that a *p*-nitro group is much more efficient than an *o*-nitro group in delocalizing a negative charge.[1,2]



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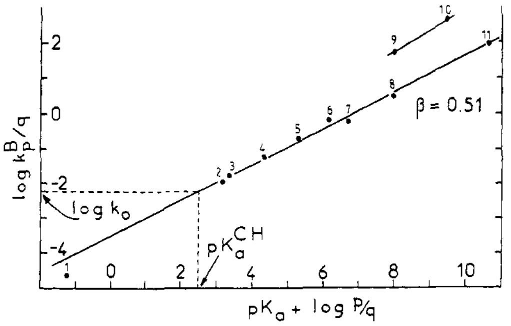

Figure 4. Statistically corrected Brönsted plot for the deprotonation of **3** by various bases in aqueous solution: $t = 25$ °C, $I = 0.1$ M. The numbering of the catalysts is indicated in Table I.

Table II. Intrinsic Reactivity of Various Carbon Acids in Aqueous Solution

carbon acid	pK_a^{CH}	log k_0	$\Delta G_0^\ddagger$, kJ mol^{-1}	ref
$CH_2(CN)_2$	11.1	$7^{a,d}$	33	23
9-cyanofluorene	10.71	$3.62^{a,c,e}$	52.2	43
CH_3NO_2	10.28	$-0.59^{a,d}$	76.3	26
$CH_3COCH_2COCH_3$	9.11	$1.90^{a,e}$ $2.75^{a,d}$	62	14a
1,3-indandione	7	$2.27^{a,e}$ $3.13^{a,d}$	60	14b
$C_6H_5CH_2NO_2$	6.77	$-1.22^{a,d}$	80	26
$CH_3CH(NO_2)_2$	5.24	$1^{a,f}$	67	22
3	2.50	$-2.15^{b,f}$	85.5	this work

[a] $t = 20$ °C. [b] $t = 25$ °C. [c] 90% H_2O–10% Me_2SO. [d] Ionization by secondary amines. [e] Ionization by primary amines. [f] Ionization by carboxylate ions.

A noteworthy feature is that the high acidity of **3** is mainly the result of an exceptionally low tendency of the resulting carbanion C-3 to undergo reprotonation by any general acid, including hydronium ion ($k_{-p}^{H} = 0.43$ L mol^{-1} s^{-1}). The situation is best appreciated by comparing the rate and equilibrium constants for the ionization of **3** according to the simplified equilibrium 12 (see Table I) to the similar parameters determined for the ionization of TNT in a 50:50 (v/v) H_2O–dioxan mixture: $k_p^{OH} = 2.42$ L mol^{-1} s^{-1}; $k_{-p}^{H_2O} = 7.5 \times 10^{-3}$ s^{-1}; $K_p = k_p^{OH}/k_{-p}^{H_2O} = 323$ L mol^{-1}.[29] From these data, one obtains the ratios

$$\mathbf{3} + OH^- \underset{k_{-p}^{H_2O}}{\overset{k_p^{OH}}{\rightleftharpoons}} \text{C-3} + H_2O \qquad (12)$$

$k_p^{OH}(\mathbf{3})/k_p^{OH}(\text{TNT}) \approx 500$, $k_{-p}^{H_2O}(\text{TNT})/k_{-p}^{H_2O}(\mathbf{3}) \approx 2 \times 10^6$, and $K_p(\mathbf{3})/K_p(\text{TNT}) \approx 10^9$, which clearly show that the changes in the equilibrium constant K_p for carbanion formation are primarily the reflection of those in the rate constant $k_{-p}^{H_2O}$ for carbanion reprotonation by the water molecules. Interestingly, the 10^{10}-fold higher stability of the DNBF–hydroxide σ-adduct **1a** relative to its TNB analogue **2a** was found to derive essentially from a very slow rate of spontaneous decomposition: the ratio $k_{-2(TNB)}/k_{-2(DNBF)}$ is about 4×10^6, a value which is nearly the same as that of the above $k_{-p}^{H_2O}(\text{TNT})/k_{-p}^{H_2O}(\mathbf{3})$ ratio. This suggests that the high stability of the carbanion C-3 has the same origin as that of the σ-adducts **1a** and **1b** and arises for the most part from an extensive delocalization of the negative charge over the nitro groups and the furoxan ring (resonance structures A–D). The olefinic character of the exocyclic carbon is in fact confirmed by the finding of two nonequivalent methylene protons in the ^1H NMR spectrum of C-3 in Me_2SO ($\delta_{H5} = 8.78$, $\delta_{Ha} = 6.60$, $\delta_{Hb} = 6.42$, $J_{HaHb} = 0.9$, $J_{HbH5} = 0.9$).[37]

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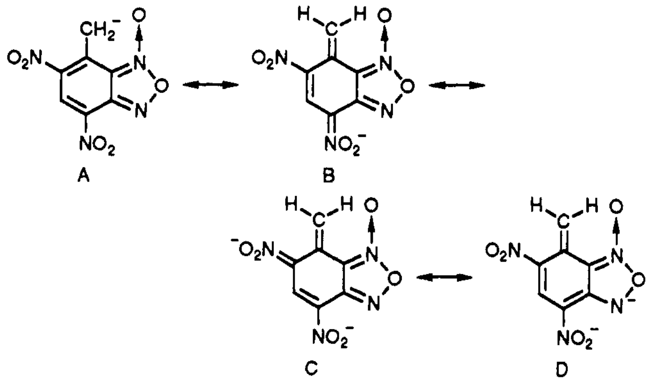
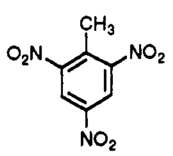
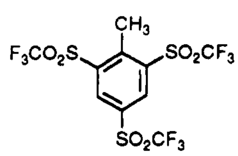


Figure 4 shows the statistically corrected Brönsted plot pertaining to the base catalysis of the deprotonation of **3**. An interesting but probably fortuitous feature is that the points for the TES and CAPS buffers which act as secondary amine buffers fall satisfactorily on the Brönsted line defined by carboxylate ion buffers. In general, secondary amines are somewhat more efficient catalysts than $RCOO^-$ ions in the ionization of carbon acids[12,14,15,18,38] but cases where the reactivity difference between these two classes of catalysts is small are known, e.g., the ionization of acetylacetone in 90% H_2O–10% Me_2SO.[14a] Also, it is perhaps important to note that most available data regarding the behavior of secondary amines in proton-transfer reactions to or from carbon refer to two alicyclic amines, namely, piperidine and morpholine.[12] Unfortunately, the use of these two amines, as well as of common primary amines like butylamine or methoxyethylamine, was precluded in reaction 4 by the high tendency of these catalysts to act as nucleophiles, undergoing preferentially covalent addition at the 7-position of **3** to give σ-adducts of type **6**. Such addition reactions of amines have not been observed at the methyl-bearing carbon of TNT but they have been reported to occur in related benzylic systems, e.g., 2,4,6-trinitrobenzyl chloride, affording the adducts **7**, and 2,2′,4,4′6,6′-hexanitrobibenzyl, giving the adducts **8**.[39,40] On the other hand, the finding that phenoxide buffers are much more reactive catalysts than $RCOO^-$ ions in reaction 3 is consistent with all previous observations in aqueous Me_2SO solutions.[12-15,17,18,38] Similarly, the deviations of the points for deprotonation of **3** by hydroxide ion (not shown) and water from the Brönsted line of Figure 4 are in the range typical for proton-transfer reactions at carbon.[26,41]


TNT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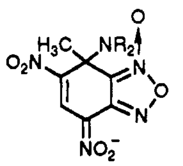
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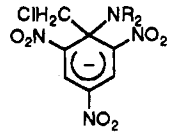
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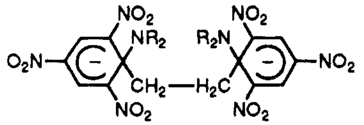
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The β_B value deduced from the lines of Figure 4 is equal to 0.51 (0.58 from the two phenoxide points), comparing well with those generally observed in the deprotonation of carbon acids and suggesting that the proton transfer is essentially half-complete at the transition state.[12,14,15] Also, this value shows that there is no particular leveling effect on catalyst efficacy, supporting our idea that the importance of the solvent pathway observed in reaction 4 is directly a consequence of the high acidity of **3**. The Brönsted plots also allowed a determination of the intrinsic rate constant ($k_0 = k_p^B/q$ at $pK_a^{BH} - pK_a^{CH} + \log p/q = 0$) of the Marcus theory[42] for the ionization of **3**: $\log k_0 = -2.15$ at 25 °C. This is a very low value for such a strong carbon acid, a value which is comparable with those found for the ionization of much weaker carbon acids like phenylnitromethane or nitromethane in aqueous solution (Table II).[26] As has been discussed recently by various authors,[12-19,26] such low k_0 values for nitro-activated carbon acids are commonly the reflection of the important structural–electronic–solvational reorganization which is required to form a carbanion with an extensive delocalized negative charge. The high intrinsic energy barrier ($\Delta G_0^\ddagger = 85.5$ kJ mol^{-1}) associated with reaction 4 confirms our earlier suggestion of an exceptional stabilization of the carbanion C-3 through delocalization of the negative charge onto the two nitro groups and the furoxan ring. It also suggests that this structural reorganization is not synchronous with the proton transfer but lags behind it in the deprotonation reaction.[12,14,43]

In this respect, it is interesting to come back to the aforementioned observation that the 10^9-fold higher acidity of **3** relative to TNT is essentially the result of a much slower rate of reprotonation of C-3 than of the TNT carbanion. The finding that the ratio $k_p^{OH}(3)/k_p^{OH}(\mathrm{TNT})$ is considerably smaller than the ratio $k_{-p}^{H_2O}(\mathrm{TNT})/k_{-p}^{H_2O}(3)$ can in fact be interpreted to mean that the intrinsic barrier for the formation of C-3 is higher than that for the deprotonation of TNT. This would be consistent with the notion that C-3 enjoys a greater amount of resonance than the TNT anion but that this enhanced resonance is only minimally felt in the transition state.

Experimental Section

Materials. 4,6-Dinitro-7-methylbenzofuroxan (**3**) was prepared by nitration of 4-nitro-7-methylbenzofuroxan, according to the method described by Drost:[44] mp 125–126 °C (lit.[44] mp 123 °C). All buffers used for rate and equilibrium measurements were commercial products which were purified according to standard procedures.

Rate and pH Measurements. Stopped-flow and conventional rate determinations were performed on a Durrum–Gibson stopped-flow spectrophotometer and a Shimadzu UV-160 spectrophotometer, respectively, with cell compartments maintained to 25 ± 0.1 °C with a thermostat. The observed rate constants used to derive the kinetic parameters listed in Tables I and S1 are average values of two or three independent determinations. The reactions were monitored at either λ_{max} of **3** (415 nm) or λ_{max} of the conjugated carbanion C-3 (480 nm).

All pH measurements were performed on a Tacussel Isis 20000 electronic pH-meter according to standard methods.

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Registry No. 3, 19262-17-0.

Supplementary Material Available: Observed first-order rate constants k_{obsd} for the ionization of 3 at zero buffer concentration in aqueous solution (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Resolution and Enantiomerization Barrier of Tetramesitylethylene

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The ^{1}H NMR spectrum of tetramesitylethylene (2) was analyzed, and the signals were assigned by means of a 2D NOESY spectrum. Attempts to observe anisochrony of the enantiotopic groups of a racemic mixture of 2 in a chiral solvent by ^{1}H NMR were unsuccessful. Molecular mechanics and MNDO calculations satisfactorily reproduce the ground-state conformation. The calculated barrier for the enantiomerization process is 21.8 (MM2) and 28.2 (MNDO) kcal mol^{-1}. 2 was chromatographically resolved on a (+)-poly(triphenylmethyl)methacrylate (PTrMA) column. Its specific rotation is $[\alpha]^{25} = -12100°$ at 365 nm and $-2300°$ at 589 nm (D line). The activation parameters for the enantiomerization of 2 in perhydrofluorene are $\Delta G^{\ddagger} = \Delta H^{\ddagger} = 39.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0$ cal mol^{-1} K^{-1}. The barrier for 2 is the highest determined experimentally for a correlated rotation.

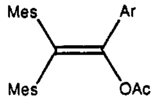
Introduction

Polyaryl-substituted compounds in which the aryl rings are attached to a central atom usually exist in a conformation where all the rings are twisted in the same sense in relation to a reference plane.[1] Such systems are dubbed "molecular propellers". If all the rings are identical and have local C_2 axes they exist in two enantiomeric forms differing in their helicity.[2] When the aryl rings are on a double bond a "vinyl propeller" results.[3-6]

Helicity reversal in molecular propellers usually involves correlated rotation of the rings. It is usually discussed in terms of "flip" mechanisms,[1,2,7] where none, some, or all the aryl rings "flip", i.e., rotate conrotatorily and pass through the plane normal to the reference plane while the nonflipping rings rotate disrotatorily and pass through the reference plane. These mechanisms are dubbed "[*n*]-ring flips", where *n* is the number of flipping rings. When all the rings are identical and have local C_2 axes any flip mechanism results in enantiomerization, and the barrier of lowest activation energy (threshold mechanism) is the enantiomerization barrier of the system.

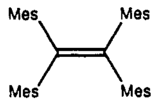
For Ar_3X and Ar_3XY (X = C, B, N) molecular propellers where all the rings are identical and have a C_2 axis, only a single example of resolution of "helicity" enantiomers has been reported.[8] Even in the crowded trimesitylmethane the enantiomerization barrier is only 21.9 kcal mol^{-1}; i.e., the half life of racemization is ca. 2 h at 0 °C.[9] The more crowded perchlorotriphenylamine has an enantiomerization barrier of 31.4 ± 0.7 kcal mol^{-1} and has been successfully resolved.[8] The propeller-shaped 1,1,2,2-tetrakis(2,6-dimethyl-4-methoxyphenyl)- and 4-(hydroxyphenyl)ethanes were resolved by chromatography on triacetylcellulose.[10]

The reported barriers for helicity reversal for the diaryl- and triarylvinyl propellers are relatively low. For example, for the crowded trimesitylethenol[3] and trimesitylethylene[11] the threshold barriers are 18.4 and 16.8 kcal mol^{-1}, respectively. This precludes the isolation of conformationally stable helicity enantiomers at room temperature. The residual enantiomers[12] of the triarylvinyl system 1,[13] in which the resolution is possible due to the desymmetrization of the α-ring, were recently resolved. 1 exists in four stereoisomeric forms (two pairs of enantiomers), and the threshold three-ring flip route led to diastereomerization and not to enantiomerization. Even when the three-ring flip mechanism is fast at the laboratory time scale, two (residual) enantiomers can be isolated. Recently, the residual enantiomers of a Ar_3CH system (tris(2′-methylbenzimidazol-1-yl)methane) were resolved.[14]



1

Mes = 2,4,6-$Me_3C_6H_2$
Ar = 2,4,6-Me_3-3-OMe-C_6H



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‡ Nagoya University.

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