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Transition State Imbalances in the Deprotonation of Picrylacetophenones by Carboxylate and Phenoxide Bases

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The kinetics of the reversible deprotonation of 4-X-substituted picrylacetophenones **3a**−**c** (X = NO_2, H, MeO) by a variety of bases have been measured in 50% H_2O−50%Me_2SO (v/v) at 25 °C. Comparison of Bronsted β_B values for the ionization of each carbon acid by phenoxide and carboxylate bases and α_{CH} values for deprotonation of **3a**−**c** by individual buffers bases indicates that the reaction proceeds through strongly imbalanced transition states. The intrinsic reactivities of **3a**−**c**, as determined from the Bronsted plots for phenoxide ion reactions, are typical for the formation of resonance-stabilized polynitrobenzyl-type carbanions, but the intrinsic rate constant k_0 decreases regularly on going from the less acidic *p*-methoxyacetophenone derivative **3c** to the more acidic *p*-nitroacetophenone derivative **3a**. This trend is attributed to the fact that the contribution of the benzoyl moiety to the resonance stabilization of the resulting carbanion **C-3** is completely negligible for the *p*-methoxy compound but not for the *p*-nitro compound. An extensive ^{1}H and ^{13}C NMR study of the ionization of **3a**−**c** confirms this proposal, with steric hindrance to rotation of the picryl ring around the C_α−C_{ipso} linkage being observed at the probe temperature in the *p*-methoxy-substituted carbanion **C-3c**, at −40 °C for the unsubstituted carbanion **C-3b**, but not at all for the *p*-nitro carbanion **C-3a**. A major finding, however, is that the three carbanions undergo protonation at the *p*-nitro group of the picryl ring to form nitronic acids in acidic media. This behavior clearly shows that charge delocalization through the 2,4,6-trinitrophenyl moiety is predominant in the three systems, including **C-3a**.

Introduction

It has now been clearly demonstrated that the intrinsic reactivity (in the Marcus sense) of a carbon acid is closely related to the extent of the structural and solvational reorganization that is needed to form the conjugate carbanion.[1] The greater the importance of the resonance stabilization of the carbanion is, the greater the lag with which it develops behind proton transfer along the reaction coordinate and the lower the intrinsic reactivity of the carbon acid. On these grounds, determination of the intrinsic reactivities of carbon acids of various structural types can help clarify the electronic mode of action of substituents or moieties whose resonance capability is still subject to discussion.[2−4]

In this context, we have recently studied benzylic-type structures whose ionization affords conjugate carbanions with a high potentiality of delocalization of the negative charge through remote electron-withdrawing groups.[5] Illustrative systems are the ionization reactions of 2,4,4′-trinitro- and 2,2′,4,4′-tetranitrodiphenylmethanes **1a** and **1b** with a variety of bases of 50% H_2O−50% Me_2SO (v/v). These reactions actually proceed through strongly imbalanced transition states, exhibiting intrinsic energy barriers which are among the highest so far measured for ionization of carbon acids in aqueous solution.[5,6] The results were accounted for on the basis of the planar structure of the resulting carbanions **C-1a** and **C-1b**, respectively, which allow extensive delocalization of the negative charge over the two phenyl rings, as shown in structures A−D.[6] Low to extremely low intrinsic reactivities were also found for the ionization of the penta- and hexanitrodiphenylmethanes **1c** and **1d** as well as for that of the series of polynitrotriphenylmethanes **2a**−**2d**.[5b,c] Although steric factors prevent mutual coplanarity of the phenyl rings in the conjugate carbanions **C-2a**−**d**, all the results obtained emphasized that nitro-substituted phenyl moieties are very effective at resonance stabilization of these species.

In this paper, we report a structural and kinetic study of the ionization of the three 4-X-substituted picrylacetophenones **3a**−**c** to give the carbanions **C-3a**−**c** in 50% H_2O−50% Me_2SO (v/v) or Me_2SO solutions. It will be shown that the strong π-acceptor capability of the 2,4,6-trinitrophenyl moiety is the major factor determining the low intrinsic reactivity of **3a**−**c** but also that the

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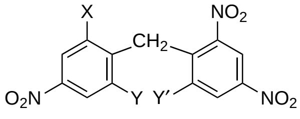

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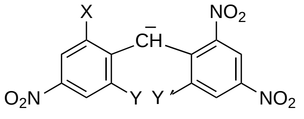
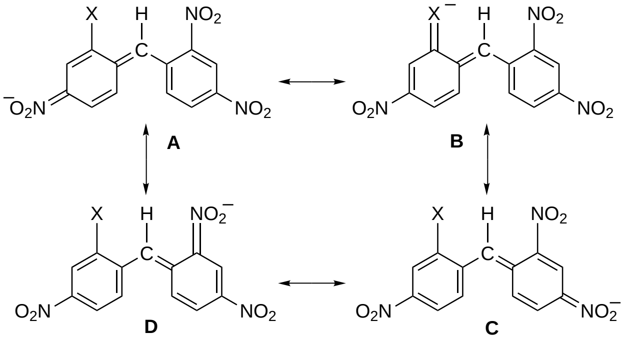
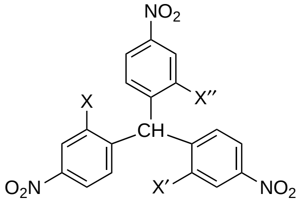


C-1

(a) X = Y = Y′ = H
(b) X = NO2, Y = Y′ = H
(c) X = Y = NO2, Y′ = H
(d) X = Y = Y′ = NO2





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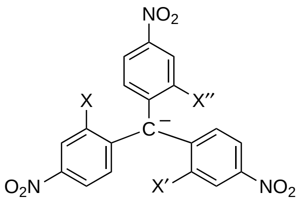
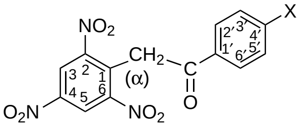


C-2

(a) X = X′ = X″ = H
(b) X = NO2, X′ = X″ = H
(c) X = X′ = NO2, X″ = H
(d) X = X′ = X″ = NO2

role of the X-substituted benzoyl moiety is important in governing some particular aspects of the acid−base behavior of **3a**−**c**, especially the thermodynamic acidity.



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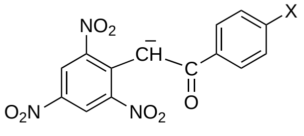
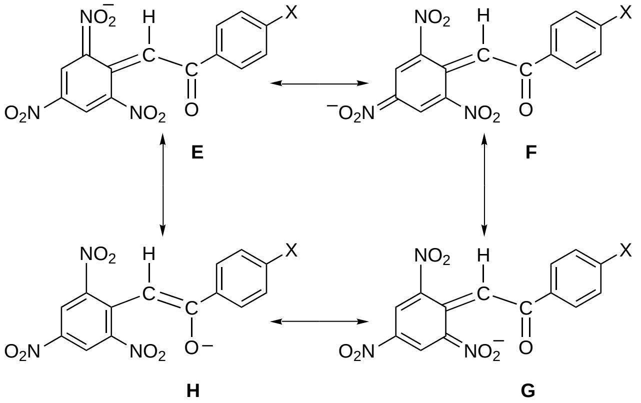


C-3

(a) X = NO2; (b) X = H; (c) X = OCH3

Results

Structural Studies. Addition of dilute tetramethylammonium hydroxide to ~3 × 10^{-5} M solutions of **3a**−**c** in 50% H_2O−50% Me_2SO results in the complete formation of purple species exhibiting intense absorption maxima at 528, 517, and 495 nm, respectively. These λ_{max} are typical for the formation of polynitrobenzyl-type carbanions.[5,7−10] Unambiguous evidence that base addition to **3a**−**c** affords the carbanions **C-3a**, **C-3b**, and **C-3c** was obtained by carrying out a ^1H and ^{13}C NMR study of the ionization reactions in Me_2SO-d_6 and acetonitrile-d_3. The most pertinent data are summarized in Tables 1 and 2. A major finding is that there is a nonequivalence of the $H_{3,5}$ protons as well as of the $C_{2,6}$ and $C_{3,5}$ carbons of the picryl ring of the *p*-methoxy-substituted carbanion **C-3c** at probe temperature. Similarly, a nonequivalence of the $H_{3,5}$ protons is observed in the ^1H spectra of the monosubstituted carbanion **C-3b** recorded at −40 °C in acetonitrile. As will be elaborated further in the discussion, NMR data favor structures E−G as the main resonance contributors for **C-3a**−**c**.



Kinetic and Equilibium Measurements. All rate and equilibrium measurements pertaining to the ionization of **3a**−**c** (eq 1) were made in 50−50 (v/v) H_2O−Me_2SO at 25 °C and constant ionic strength of 0.5 M maintained with NMe_4Cl. Pseudo-first-order conditions were used throughout with a large excess of the acid (HCl), base (NMe_4OH), or buffer (carboxylic acids, phenols) reagents over the picrylacetophenone concentration ([**3**] ≈ 3 × 10^{-5} M).

The pK_a^{CH} values of **3a**−**c** were first determined from observed absorbance variations at λ_{max} of **C-3a**−**c** obtained at equilibrium as a function of pH. These described clear acid−base equilibrations, as evidenced by Figure S1[11] which shows that excellent straight lines with unit slopes were obtained on plotting the log values of the ratio of the concentrations of ionized to nonionized acetophenones as a function of pH (eq 2). We thus readily obtained the following: $pK_a^{CH} = 5.71$ for **3a**; $pK_a^{CH} = 7.80$ for **3b**; $pK_a^{CH} = 10.19$ for **3c** (Table 4). Depending upon

$$\mathbf{3a-c} \xrightleftharpoons[k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] + k_{-p}^{H_2O}]{k_p^{H_2O} + k_p^{B}[B] + k_p^{OH}[OH^-]} \mathbf{C\text{-}3a-c} \qquad (1)$$

$$\log [\mathbf{C\text{-}3}]/[\mathbf{3}] = pH - pK_a^{CH} \qquad (2)$$

$$k_{obsd} = k_p^{H_2O} + k_p^{B}[B] + k_p^{OH}[OH^-] + k_{-p}^{H_2O} + k_{-p}^{BH}[BH] + k_{-p}^{H}[H^+] \qquad (3)$$

the pH studied, the kinetics of the interconversion of **3**

Table 1. ^1H Chemical Shifts for Picrylacetophenones 3a−c and Related Carbanions C-3a−c in Me_2SO-d_6 and Acetonitrile-d_3[a]

substituent X	compd	$\delta_{H3,5}$	$\delta_{H\alpha}$	$\delta_{H2',6'}$	$\delta_{H3',5'}$	$\delta_{H4'}$	δ_{OCH3}
NO_2	**3a**	9.13 (9.02)	5.17 (5.05)	8.31 (8.24)	8.44 (8.39)		
	C-3a	8.52 (8.56)	7.13 (7.11)	8.00 (8.02)	8.29 (8.23)		
H	**3b**	9.12 (9.23)	5.07 (5.00)	8.07 (8.06)	7.61 (7.59)	7.71 (7.73)	
	C-3b	8.46 (8.54)[b]	7.26 (7.24)	7.80 (7.84)	7.47 (7.46)	7.47 (7.46)	
OCH_3	**7c**	9.10	4.99	8.04	7.11		3.88
	C-3c	8.31 8.57	7.30	7.78	7.00		3.81

[a] Internal reference Me_4Si; δ in ppm; values in parentheses refer to [$^2H_3$]-MeCN. [b] A large broadening of this resonance occurs at −40 °C in acetonitrile.

Table 2. ^{13}C Chemical Shifts for Picrylacetophenones 3a–c and Related Carbanions C-3a–c[a]

X	compd	δ_{C1}	$\delta_{C2,6}$	$\delta_{C3,5}$	δ_{C4}	$\delta_{C\alpha}$	δ_{CO}	$\delta_{C1'}$	$\delta_{C2',6'}$	$\delta_{C3',5'}$	$\delta_{C4'}$	δ_{OCH3}
NO_2	**3a**	130.82	150.85	123.77	146.72	39.59	193.00	139.90	129.82	124.13	150.49	
	C-3a	133.26	141.82	124.53	129.56	92.95	180.97	146.82	128.16	123.66	148.36	
H	**3b**	131.41	150.94	123.63	146.6	39.11	193.51	135.34	128.4	129.4	134.16	
	C-3b	132.23	140.88	124.71	127.74	95.32	184.53	140.88	127.05	128.33	130.88	
OCH_3	**3c**	131.52	150.94	123.48	146.52	38.63	191.69	128.18	130.82	114.23	163.89	55.72
	C-3c	131.64	138.00 142.00	124.83[c]	127.08	96.33	184.13	133.35	129.14	113.60	161.67	55.34

[a] Internal reference Me_4Si; δ in ppm, J in Hz. [b] $J^{3a}_{C_\alpha H_\alpha} = 132.5$; $J^{C\text{-}3a}_{C_\alpha H_\alpha} = 159$; $J^{3b}_{C_\alpha H_\alpha} = 132.3$; $J^{C\text{-}3b}_{C_\alpha H_\alpha} = 158.9$; $J^{3c}_{C_\alpha H_\alpha} = 132.7$; $J^{C\text{-}3c}_{C_\alpha H_\alpha} = 158.6$. [c] Broad signal.

Table 3. Rate Constants for the Ionization of the Picrylacetophenones 3a–c in 50% H_2O–50% Me_2SO (v/v)[a]

			3a		**3b**		**3c**	
buffer (basic species)	no.	pK_a^{BH}[b]	k_p^B (M^{-1} s^{-1})	k_{-p}^{BH} (M^{-1} s^{-1})	k_p^B (M^{-1} s^{-1})	k_{-p}^{BH} (M^{-1} s^{-1})	k_p^B (M^{-1} s^{-1})	k_{-p}^{BH} (M^{-1} s^{-1})
H_2O	1	−1.44	7.21×10^{-4} [b]	10200[c]	1.73×10^{-5} [b]	30300[c]	1.64×10^{-7} [b]	70 175[c]
chloroacetate ion	2	3.71			0.61	7600		
formiate ion	3	4.45			2.04	4570		
methoxyacetate ion	4	4.65			1.95	2750		
acetate ion	5	5.78			6.30	660		
2,6-dichlorophenoxide ion	6	7.40					28.7[d]	17 750
2-cyanophenoxide ion	7	7.97	820	4.50[d]	218	158	48[d]	7950
4-cyanophenoxide ion	8	8.45	1250	2.27[d]	316	63	110[d]	6020
2-bromophenoxide ion	9	9.52	4480	0.69[d]	1000	19[d]	267	1250
4-chlorophenoxide ion	10	10.18	10 600	0.36[d]	2510	10.47[d]	480	540
phenoxide ion	11	11.21	25 000	0.17[d]	5000	1.94[d]	1320	130
4-methoxyphenoxide ion	12	11.47			5500	1.17[d]		
OH^-	13	17.34	55 600[e]	1.42×10^{-7} [f]	13 660[e]	4.31×10^{-6} [f]	2190[e]	1.69×10^{-4} [f]

[a] $I = 0.5$ M NMe_4Cl; $t = 25$ °C; experimental error in the rate constants: ±4% or better; in pK_a^{BH} and pK_a^{CH}: ±0.05 pK units; in the rate constants calculated from eq 4: ±10%; pK_a^{BH} values from ref 5a,b. [b] $k_p^{H_2O}/27.6$ with $k_p^{H_2O}$ calculated from $K_a^{CH}k_{-p}^{H}$. [c] $k_{-p}^{BH} = k_p^{H}$. [d] Calculated from k_p^B or k_{-p}^{BH} via eq 4. [e] $k_p^B = k_p^{OH}$. [f] $k_{-p}^{H_2O}/27.6$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with $pK_s = 15.83$ at 25 °C (see text).

and **C-3** was studied by mixing a neutral solution of **3a–c** with the appropriate NMe_4OH or buffer solutions (pH ≥ pK_a^{CH}) or by mixing a freshly prepared 0.01 M NMe_4OH solution of the carbanion **C-3** with the appropriate buffer or HCl solutions (pH ≤ pK_a^{CH}). In agreement with a direct equilibrium approach according to eq 1, oscilloscope pictures obtained in stopped-flow experiments revealed that only one relaxation time is associated with the interconversion in buffer and NMe_4OH solutions of pH ≥ 4.45. In these instances, the general expression for the observed first-order rate constant pertaining to the process is given by eq 3. In this equation, the rate constants k_p^{OH}, k_p^{B}, and $k_p^{H_2O}$ refer to the deprotonation of **3a–c** by hydroxide ion, the buffer base species, and the solvent, respectively, while the rate constants k_{-p}^{H}, k_{-p}^{BH}, and $k_{-p}^{H_2O}$ refer to the reprotonation of the carbanions **C-3a–c** by hydronium ion, the buffer acid species, and the solvent, respectively.

All k_{obsd} values for ionization of **3a–c** according to eq 1 are summarized in Tables S1–S6 given as supporting information.[11] To be noted is that equilibrium (1) was approached from both reactant and product sides in buffer systems with $pK_a^{BH} \approx pK_a^{CH}$, e.g., 2-cyanophenol ($pK_a^{BH} = 7.97$) and 4-cyanophenol ($pK_a^{BH} = 8.45$) buffers in the case of **3b** ($pK_a^{CH} = 7.80$) or 2-bromophenol ($pK_a^{BH} = 9.52$), 4-chlorophenol ($pK_a^{BH} = 10.18$), and phenol ($pK_a^{BH} = 11.21$) buffers in the case of **3c** ($pK_a^{BH} = 10.19$).

From the k_{obsd} values obtained in NMe_4OH solutions, excellent straight lines fitting the reduced equation $k_{obsd} = k_p^{OH}[OH^-]$ were obtained in the three systems (not shown), which afforded the following: $k_p^{OH}{}_{(3a)} = 55\,600$ M^{-1} s^{-1}; $k_p^{OH}{}_{(3b)} = 13\,660$ M^{-1} s^{-1}; $k_p^{OH}{}_{(3c)} = 2190$ M^{-1} s^{-1}. This allowed the calculation of the $k_{-p}^{H_2O}$ rate constants from $k_{-p}^{H_2O} = k_p^{OH}\,K_s/K_a^{CH}$ where K_s is the autoprotolysis constant of the 50% H_2O–50% DMSO mixture containing 0.5 M NMe_4Cl ($pK_s = 15.83$ at 25 °C):[5a] $k_{-p}^{H_2O}{}_{(3a)} = 3.92 \times 10^{-6}$ s^{-1}; $k_{-p}^{H_2O}{}_{(3b)} = 1.19 \times 10^{-4}$ s^{-1}; $k_{-p}^{H_2O}{}_{(3c)} = 4.66 \times 10^{-3}$ s^{-1}.

Table 4. pK_a Values and Tautomerization Constants K_T for Picrylacetophenones 3a–c in 50% H_2O–50% Me_2SO[a]

	3a	**3b**	**3c**
pK_a^{CH}	5.71	7.80	10.19
pK'^{aci}_a	2.70	2.94	3.17
K_T	9.77×10^{-4}	1.38×10^{-5}	9.55×10^{-8}
% aci-form	≈0.1	$\approx 1.4 \times 10^{-3}$	$\approx 10^{-5}$

[a] $t = 25$ °C; $I = 0.5$ M NMe_4Cl.

In the various phenol and carboxylic acid buffer solutions employed to cover the pH range of 4.45–11.47, a standard treatment of the rate data showed that only the $k_p^B[B]$ and $k_{-p}^{BH}[BH]$ terms were important in determining the corresponding k_{obsd} values. All k_p^B and k_{-p}^{BH} rate constants determined for eq 1 are summarized in Table 4. For buffer solutions with $pK_a^{BH} \geq pK_a^{CH} + 1$ (or $pK_a^{BH} < pK_a^{CH} - 1$), the k_{-p}^{BH} (or k_p^B) values were calculated from the measured k_p^B (or k_{-p}^{BH}) values by means of eq 4:

$$k_p^{B} = k_{-p}^{BH} K_a^{CH}/K_a^{BH} \tag{4}$$

Oscilloscope pictures revealed that reprotonation of **C-3a**, **C-3b**, and **C-3c** in dilute HCl solutions (5×10^{-4}–5×10^{-2} M) as well as that of **C3b** in chloroacetic acid buffers (pH = 3.41–4.01) does not proceed directly according to eq 1 but involves the instantaneous formation of an intermediate species X which subsequently decomposes to **3a**, **3b**, or **3c**. The UV–vis absorption spectra of these species, whose formation is pH-dependent and essentially complete in 5×10^{-2} M HCl, could be recorded by stopped-flow spectrophotometry (Figure 1). On the grounds of analogy with the protonation behavior of the carbanion **C-1b** of 2,2′,4,4′-tetranitrodi-

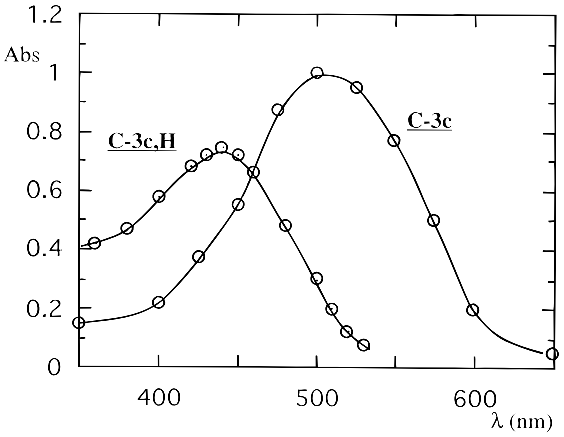
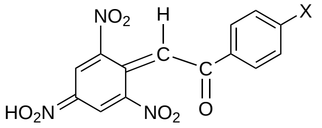


Figure 1. UV−vis absorption spectra of the carbanion **C-3a** and the related nitronic acid **C-3c**,H in a 5 × 10^{-2} M HCl solution in 50% H_2O−50% Me_2SO (v/v).

phenylmethane in methanol[12] and some other features to be discussed later, there is little doubt that the X species arise from protonation at a NO_2 group of **C-3a**−**c**, most likely at the 4-position, and are therefore the nitronic acids C-3H. Thus, the appropriate scheme for the conversion of **C-3** to **3** at low pH is shown in eq 5 and the measured k_{obsd} values for this process are expected to obey the general equation (6) in buffer solutions (Table S2) and the reduced equation (7) in HCl solutions (Table S6):[11,12]



C-3H

$$\mathbf{C\text{-}3H} \underset{}{\overset{K'_a}{\rightleftarrows}} \mathbf{C\text{-}3} + H^+ \xrightarrow{k_{-p}{}^{H}[H^+] + k_{-p}{}^{H_2O} + k_{-p}{}^{BH}[BH]} \mathbf{3} \qquad (5)$$

$$k_{obsd} = (k_{-p}{}^{H^+}[H^+] + k_{-p}{}^{H_2O})\frac{K'_a}{K'_a + [H^+]} + k_{-p}{}^{BH}[BH]\frac{K'_a}{K'_a + [H^+]} \qquad (6)$$

$$k_{obsd} = (k_{-p}{}^{H^+}[H^+] + k_{-p}{}^{H_2O})\frac{K'_a}{K'_a + [H^+]} \qquad (7)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_{-p}{}^{H}[H^+]} + \frac{1}{k_{-p}{}^{H}K'_a} \qquad (8)$$

In agreement with eq 7, curvilinear k_{obsd} vs $[H^+]$ plots were obtained from measurements in HCl solutions (not shown, see Table S6, supporting information). Taking into account that the solvent contribution ($k_{-p}{}^{H_2O}$) is negligible in the pH range at hand, eq 7 may be rewritten in the form of eq 8. In accordance with this equation, plots of $1/k_{obsd}$ vs $1/[H^+]$ afforded satisfactory straight lines (Figure 2), from which the following $k_{-p}{}^{H}$ and $k_{-p}{}^{H}$ K'_a values were determined: $k_{-p}{}^{H} = 10\,200$ M^{-1} s^{-1}, $k_{-p}{}^{H}$ $K'_a = 20.4$ s^{-1} for **3a**, $k_{-p}{}^{H} = 30\,300$ M^{-1} s^{-1}, $k_{-p}{}^{H}$ $K'_a = 34.8$ s^{-1} for **3b**, $k_{-p}{}^{H} = 70\,175$ M^{-1} s^{-1}, $k_{-p}{}^{H}$ $K'_a = 47.45$ s^{-1} for **3c**. Interestingly, the above $k_{-p}{}^{H}$ K'_a values agree well with the plateaus observed in Table S6 (supporting information). Combination of $k_{-p}{}^{H}$ and $k_{-p}{}^{H}$ K'_a afforded the following pK'_a values for ionization of the three nitronic acids: $pK'_a = 2.70$ for **C-3aH**, 2.94 for **C-3bH**, and 3.17 for **C-3cH**. From the $k_{-p}{}^{H}$ values, the $k_p{}^{H_2O}$ rate constants for deprotonation of **3a**−**c** by the solvent were also calculated as $k_p{}^{H_2O} = K_a{}^{CH}k_{-p}{}^{H}$ ($k_{p\mathbf{3a}}{}^{H_2O} = 1.99 \times 10^{-2}$ s^{-1}; $k_{p\mathbf{3b}}{}^{H_2O} = 4.77 \times 10^{-4}$ s^{-1}, and $k_{p\mathbf{3c}}{}^{H_2O} = 4.52 \times 10^{-6}$ s^{-1}).

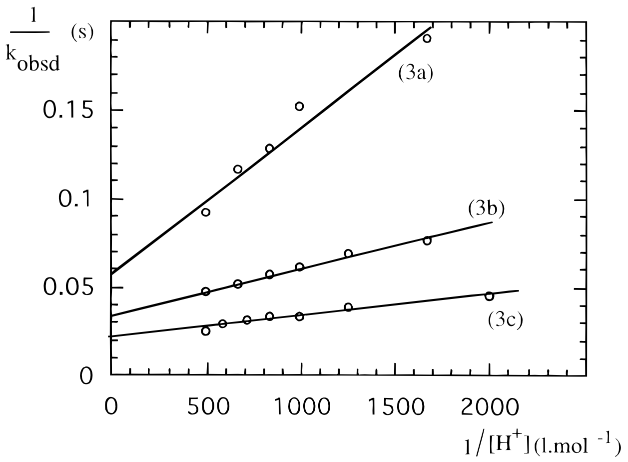


Figure 2. Inversion plots according to eq 8 for protonation of the carbanions **C-3a**−**c** in dilute HCl solutions in 50% H_2O−50% Me_2SO (v/v): $T = 25$ °C, $I = 0.5$ M NMe_4Cl.

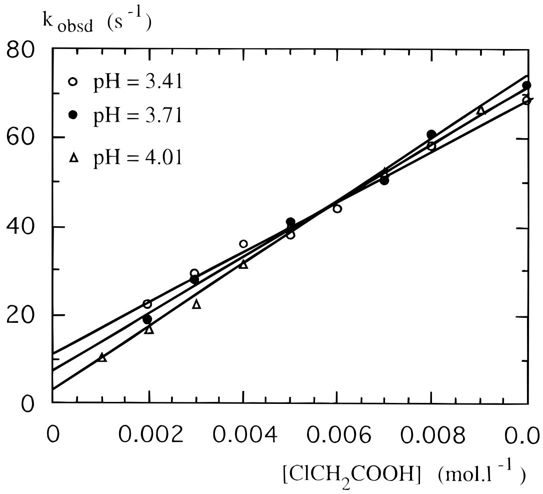


Figure 3. Effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for protonation of the carbanion **C-3b** in chloroacetic acid buffers in 50% H_2O−50% Me_2SO (v/v): $T = 25$ °C, $I = 0.5$ M NMe_4Cl.

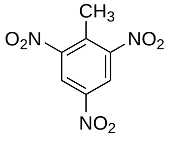
Consideration of the reprotonation of **C-3b** in chloroacetic acid buffers, eq 6 predicts that linear plots of k_{obsd} vs [BH] should be obtained at constant pH but that the slopes of these plots should decrease with increasing the H^+ concentration. As shown in Figure 3, the data obtained at the three pH studied confirmed these expectations. In addition, the values of the intercepts agreed well with estimates made from eq 7. After appropriate correction for the $K'_a/(K'_a + [H^+])$ terms, the slopes of the lines in Figure 4 afforded three consistent values for the $k_{-p}{}^{BH}$ rate constant pertaining to chloroacetic acid (Table 4). The corresponding $k_p{}^{B}$ value was calculated from eq 4.

Discussion

Structure of the Carbanions. As can be seen in Tables 1 and 2, the resonances of the exocyclic C_α and H_α atoms of **3a**, **3b**, and **3c** suffer large downfield shifts upon ionization: the $\Delta\delta(H_\alpha)$ and $\Delta\delta(C_\alpha)$ values lie in the ranges 1.96−2.31 and 53.46−57.70 ppm, respectively.

Although such $\Delta\delta$ values are mainly the result of two opposing effects,[6,13,14] namely a high-field shift caused by increased electron density at C_α and a low-field shift caused by the $sp^3 \rightarrow sp^2$ rehybridization of this carbon, the importance of the observed downfield variations shows that the rehybridization factor is largely predominant. The finding that the ionization induces large variations in $^1JC_\alpha H_\alpha$ ($\Delta J = 27$) together with the high values of these coupling constants for **C-3a**, **C-3b**, and **C-3c** are also consistent with a strong olefinic character of the C_α carbon.[15] This implies a concomitant and important delocalization of the negative charge of the carbanion either through the picryl ring (structures **E**−**G**) or through the benzoyl moiety (structure **H**).

That charge delocalization occurs preferentially through the 2,4,6-trinitrophenyl moiety, as depicted in structures **E**−**G**, is supported by the following observations: (1) the visible spectra of the carbanions **C-3a**, **C-3b**, and **C-3c** show an intense absorption maximum at wavelengths (528, 517, and 518 nm, respectively) similar to that of the 2,4,6-trinitrotoluene anion **C-4** (514 nm);[7−10] (2) the ionization of **3a**, **3b**, and **3c** induces a strong shielding of the $H_{3,5}$ protons of the picryl ring. The $\Delta\delta$(H) values lie in the range −0.61, −0.79 ppm, comparing well with the proton shifts observed in the ionization of various 2,4,6-trinitrobenzyl derivatives, including 2,4,6-trinitrotoluene (TNT) ($\Delta\delta(H_{3,5}) = -0.74$ ppm),[6,10] (3) the resonances of the $C_{2,6}$ and C_4 carbons, especially the latter, move markedly to high field, whereas those of the $C_{3,5}$ carbons move slightly to low field on going from **3a**−**c** to **C-3a**−**c**: $\Delta\delta(C_{2,6}) \approx -10$; $\Delta\delta(C_4) \approx -18$; $\Delta\delta(C_{3,5}) \approx +1$. Interestingly, the situation is reminiscent of the one reported in ^{13}C studies of the formation of the related carbanion **C-5** of 2,4,6-trinitrophenylacetone as well as of that of picryl σ-adducts of general structure **5** according to eq 9.[16−21] In these latter instances, SCFMO calculations have indicated that the σ-complexation results in increases in π-electron density at the 2, 4, and 6-ring positions as well as on the NO_2 substituents and in decreases at the 3- and 5-positions, accounting well for the observed variations in the carbon chemical shifts of the cyclohexadienyl ring: $\Delta\delta(C_{2,6}) \approx -17$, $\Delta\delta(C_4) \approx -29$, $\Delta\delta(C_{3,5}) \approx 2$.[22,25] In addition, the calculations confirmed the major role of the paraquinoid structure **6B** in the delocalization of the negative charge of the adducts.[24] Analogously, there is little doubt that the variations suffered by the carbon resonances of the picryl ring in reactions (1) suggest a major contribution of the nitronate representations E−G, especially F, to the structure of **C-3a**, **C-3b**, and **C-3c**; (4) there is a nonequivalence of the ortho and meta carbons, as well as of the $H_{3,5}$ protons of the picryl ring of the *p*-methoxybenzoyl carbanion **C-3c** at probe temperature and of the unsubstituted analogue **C-3b** at −40 °C. These last findings are clearly consistent with the high double bond character of the $C_{ipso}-C_\alpha$ bond, as shown in structures **E**−**G**. That such nonequivalence could not be observed for the carbanion **C-3a** suggests that the contribution of the enolate structure **H** to its stabilization is not totally negligible and therefore that the *p*-nitrobenzoyl moiety is capable to compete to some extent with the picryl ring in attracting the negative charge.



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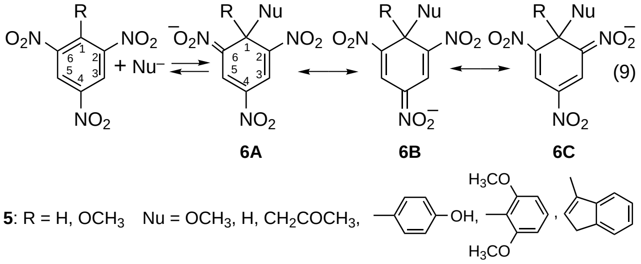
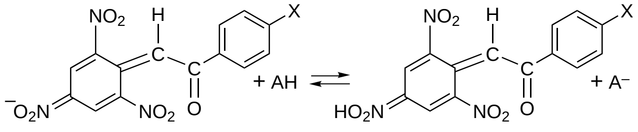
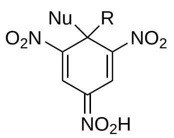


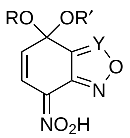
Nitronic Acid Formation. It follows from the predominance of the resonance structures **E**−**G** over **H** that the fast reversible protonation of **C-3a**−**c** in acidic solutions can only occur at a nitro group, and hence, the intermediate protonated species X observed at low pH must be nitronic acids. Furthermore, it is well known that a *p*-NO_2 group is significantly more effective at resonance stabilization of charge than is a *o*-NO_2 group.[24−26] On this basis, one can understand, as it is borne out by NMR results, that the negative charge of **C-3a**−**c** will lie preferentially on the 4-NO_2 group and that it is this group which will be preferentially protonated, allowing the identification of the X-species as the nitronic acids **C-3,H**.



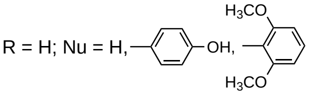
C-3 **C-3H**



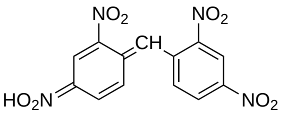
6,H



7,H



(a) Y = N, R = R′ = CH_3
(b) Y = N → O, R = R′ = CH_3
(c) Y = N, R---R′ = $-CH_2CH_2-$
(d) Y = N → O, R---R′ = $-CH_2CH_2-$



C-1b,H

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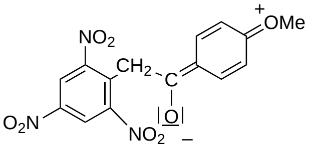
A number of nitronic acids of type **6,H** and **7,H** arising from protonation of anionic nitrocyclohexadienylide structures have been characterized in the literature.[27−29] Also, the formation of the nitronic acid **C-1b,H** upon protonation of the (2,2′,4,4′-tetranitrodiphenyl)methyl carbanion **C-1b** has been reported in methanol.[12] In all cases, the protonation results in a marked hypsochromic shift of the absorption maxima in the electronic spectra, as it is actually observed for the conversion of **C-3** to **C-3,H**: $\lambda_{max}^{\textbf{C-3a}} = 528$ nm, $\lambda_{max}^{\textbf{C-3a,H}} = 382$ nm; $\lambda_{max}^{\textbf{C-3b}} = 517$ nm, $\lambda_{max}^{\textbf{C-3b,H}} = 404$ nm; $\lambda_{max}^{\textbf{C-3c}} = 495$ nm, $\lambda_{max}^{\textbf{C-3c,H}} = 438$ nm. On the other hand, pK'_a values of the order 4.2−4.5 have been reported for formation of the nitronic acids **7H** and **C-1b,H** in methanol.[12,29] Since the acidity of oxygen acids is usually increased on going from methanolic to aqueous solutions but decreased upon addition of a dipolar aprotic solvent like Me_2SO,[30] our pK'_a values measured for the oxygen protonation of **C-3a**−**c** in 50% H_2O−50% Me_2SO compare well with previous results, giving additional support to our assignment of **C-3,H** as nitronic acids. However, the fact that the pK'_a values increase in the order **C-3a,H** < **C-3b,H** < **C-3c,H** is consistent with NMR evidence that charge delocalization through the picryl moiety decreases to some extent on going from the *p*-methoxybenzoyl derivative to the *p*-nitrobenzoyl derivative, as expected from the electronic effects of the X substituent.

Equilibrium and Kinetic Acidity of 3a−**c.** In agreement with the general observation that compounds yielding highly delocalized anions show decreased pK_a values in Me_2SO relative to water,[30] the acidity of TNT increases on going from water ($pK_a^{H_2O} = 13.6$)[31] to Me_2SO ($pK_a^{Me_2SO} = 10.5$),[32] making reasonable to estimate a pK_a value of ca. 12.5 for this carbon acid in 50% H_2O−50% Me_2SO. On this basis, Table 3 shows that substitution of one methyl hydrogen of TNT for an unsubstituted benzoyl group markedly increases the acidity: $\Delta pK_a \approx 4.7$. As expected, introduction of the electron-donating OCH_3 group in the para position of the phenyl ring decreases the acidifying effect of the benzoyl moiety, whereas that of the electron-withdrawing NO_2 group increases it. A noteworthy result, however, is that the pK_a variations define a satisfactory Hammett relationship ($\rho = 2.87$), providing that σ_p^+ rather than σ_p be used for the methoxy group (Figure S2).[11] This implies that the electronic influence of the X substituent on the acidity of **3a**−**c** is of much greater importance at the ground state level—resonance structure **8** is obviously essential in determining the stability of **3c**—than at the product carbanion level, where the role of the picryl ring in delocalizing the negative charge of the three carbanions **C-3a**−**c** is very dominant. Bunting and Stefanidis have recently suggested that ground state stabilization through structures of type **9** is responsible for the finding that substituents in the phenyl ring induce a large effect upon the acidity of 4-phenacylpyridines and 4-phenacylpyridinium cations.[3c] The importance of resonance contributors like **8** and **9** is also consistent with recent conclusions that have been drawn from theoretical calculations of the electron density distributions in carbonyl-containing functional groups.[33,34]



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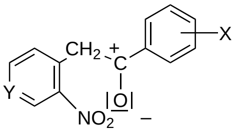
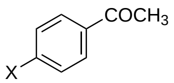


9 (Y = N, NR⁺)



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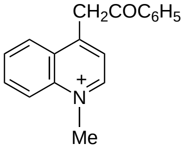
(a) X = NO2
(b) X = H
(c) X = OCH3



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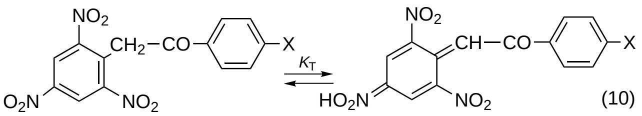
$pK_a^{H_2O}$ values of 16.70, 18.24, and 19 have been reported for the parent acetophenones **10a**−**c** of **3a**−**c**.[35−37] Neglecting the enhancing effect of Me_2SO on the pK_a values measured for **3a**−**c** in 50% H_2O−50% Me_2SO,[30] the acidifying effect due to the substitution of a methyl hydrogen of **10a**−**c** for a picryl ring appears to be of about 10 p*K* units. This makes the acidity of **3a**−**c** of the same order as that of phenacylpyridinium derivatives of type **9** ($Y = NR^+$)[3] as well as of compounds like **11** ($pK_a = 7.02$). β-Diketone derivatives like acetylacetone ($pK_a^{H_2O} = 9.11$ and $pK_a^{50\%Me_2SO} = 9.12$ at 20 °C)[38] or dibenzoylmethane ($pK_a^{50\%Me_2SO} = 8.72$ at 20 °C)[26] also have similar pK_a^{CH} values in aqueous solution.

From the pK_a^{CH} and pK'_a values pertaining, respectively, to the deprotonation of **3a**−**c** and nitronic acid formation from the conjugate carbanions, the equilibrium constants measuring the extent of the conversion of the three picrylacetophenones into their aci-forms in 50% H_2O−50% Me_2SO (eq 10) can be calculated. The data are summarized in Table 4. As can be seen, K_T and hence the aci content is very small, even for the more acidic *p*-nitroacetophenone substrate. This is in agreement with the failure to detect the presence of **C-3,H** in ^1H and ^{13}C NMR spectra recorded under common experimental conditions in Me_2SO-d_6.



(10)

Figure 4 shows statistically corrected Brönsted plots for the deprotonation of **3b** by carboxylate and phenoxide ions while Figure S3[11] shows the same relationships for deprotonation of **3a** and **3c** by phenoxide ions. For a given $\Delta pK + \log(p/q)$ value, Figure 4 exemplifies the reactivity order $ArO^- > RCOO^-$ ions, consistent with the general observation that aryl oxide ions are less solvated and therefore more efficient catalysts than carboxylate ions of the same pK_a's in proton transfer reactions at

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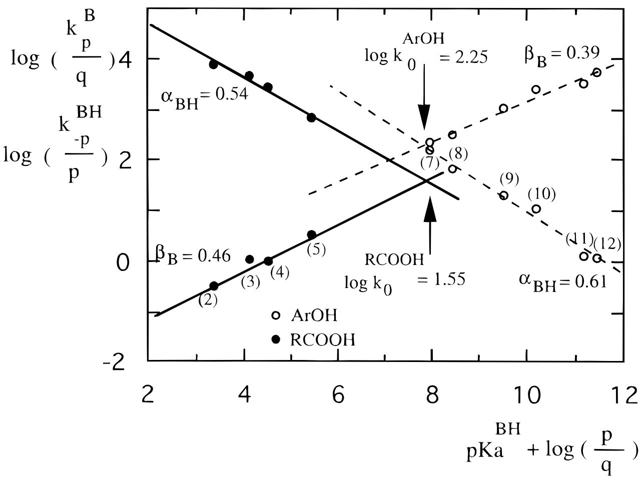

Figure 4. Brönsted plots for ionization of **3b** by carboxylate and phenoxide ions in 50% H_2O–50% Me_2SO (v/v): T = 25 °C, I = 0.5 M NMe_4Cl. The numbering of the various catalysts is given in Table 3.

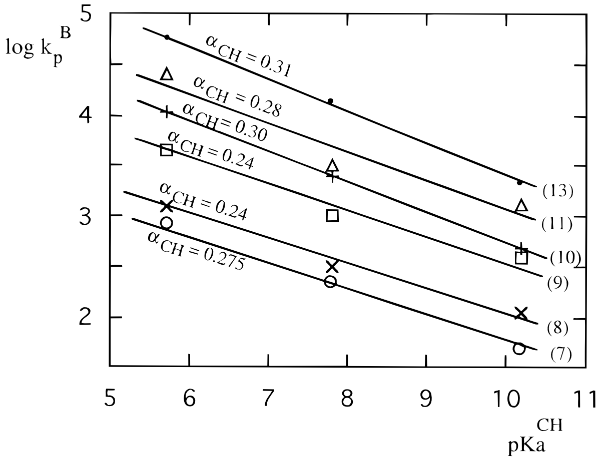

Figure 5. Effect of the acidity of the carbon acids **3a**–**c** on the rate constant of deprotonation by various phenoxide bases (entries 7–11 in Table 3) and OH^- (entry 13 in Table 3).

carbon.[5] All Bronsted β_B reported in Table 5 are in the range 0.5 ± 0.1 commonly found for the ionization of carbon acids, suggesting that proton transfer is about half-complete at the transition states of reactions (1). To be noted, however, is that β_{ArO} does not decrease regularly on going from the less thermodynamically favored protonation reaction (**3c**) to the more thermodynamically favored system (**3a**). Failure of the reactivity–selectivity principle in accounting for data pertaining to the ionization of carbon acids has often been noted by various authors.[1,39]

Our kinetic data also allow a determination of the Brönsted α_{CH} values measuring how the rate of deprotonation by a given base depends on the acidity of the carbon acid. Although they are only based on the three points pertaining to **3a**, **3b**, and **3c**, the various log k_p^B vs pK_a^{CH} plots are satisfactorily linear with slopes (α_{CH}) in the range 0.28 ± 0.03 (Figure 5). Clearly, such low α_{CH} values do not agree with the transition state picture provided by the β_B values, a situation which suggests that the ionization reactions of the three picrylacetophenones **3a**–**c** proceed through imbalanced transition states in which the development of resonance of the carbanions lags behind charge transfer.[1–5,40–42] Measuring the extent of the imbalance as $I = \alpha_{CH} - \beta_B$,[1] then negative values of the order of −0.17 ± 0.03 are calculated. Although much greater imbalances have been reported in various carbon acid systems,[1c] such I values clearly indicate that the deprotonation of **3a**–**c** gives rise to strongly resonance-stabilized carbanions, supporting a predominant role of the picryl moiety in the delocalization of the negative charge.

Table 5. Bronsted Coefficients and Intrinsic Rate Constants for the Ionization of the Picrylacetophenones 3a–c by Carboxylate and Phenoxide Bases in 50% H_2O–50% Me_2SO[a]

	3a	3b	3c
α_{CH}	0.28	0.28	0.28
β_{ArO}	0.49	0.39	0.44
β_{RCOO}		0.46	
log k_0^{ArO}	1.80	2.25	2.73
log k_0^{RCOO}		1.55	

[a] t = 25 °C; I = 0.5 M NMe_4Cl.

In the last decade it has been clearly recognized that imbalanced transition states are characteristic for the ionization of carbon acids exhibiting a low intrinsic reactivity.[1] Values of the intrinsic rate constants k_0 (in the Marcus sense)[43] for **3a**–**c**, as determined from the Brönsted plots of Figures 4 and S3 (supporting information) as $k_0 = k_p^B/q$ when $pK_a^{BH} + \log(p/q) = pK_a^{CH}$ are given in Table 5. As can be seen, the intrinsic reactivity of **3a**–**c** increases on going from the *p*-nitroacetophenone derivative **3a** (log k_0^{ArO} = 1.80) to the unsubstituted analogue **3b** (log k_0^{ArO} = 2.25) to the *p*-methoxyacetophenone compound (log k_0^{ArO} = 2.73). Thus, in agreement with our finding of smaller α_{CH} than β_B values and therefore of negative I values, it is the less acidic compound which has the highest intrinsic reactivity. Taking into account that log k_0 values for aryl oxide ion catalysts are generally greater than log k_0 values for carboxylate ions and primary amines by about 0.8 and 1.7 log unit, respectively,[5] it appears from Table 6 that the intrinsic reactivities of **3a**–**c** are about 2 orders of magnitude lower than those of β-dicarbonyl compounds of similar pK_a's, like acetylacetone and 1,3-indandione.[38,41b] This result can be accounted for only if the picryl ring contributes dominantly to the delocalization of the negative charge of **C-3a**–**c**, as shown in the resonance structures **E**–**G**. However, the finding of a lower k_0 value for the *p*-nitroacetophenone compound confirms our previous suggestion that in this case the enolate contributor H does not have a negligible influence in the delocalization of the negative charge of **C-3a**. Interestingly, the log k_0^{ArO} value for **3a** is essentially the same as that for the carbanion **C-1d** derived from (2,2′,4,4′,6,6′-hexanitrodiphenyl)methane in which steric factors have been shown to allow conjugation of the sp^2-hybridized

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Table 6. Comparison of Intrinsic Rate Constants for Deprotonation of Some Representative Carbon Acids in 50% H_2O−50% Me_2SO at 25 °C

CH acid	base	log k_0
$RCH(CN)_2$	RR′NH	≈7[a]
$CH_3COCH_2COCH_3$	$RCOO^-$	3.80[b]
	ArO^-	(4.60)[b,c]
1,3-indandione	$RCOO^-$	3.18[d]
	ArO^-	4[d]
3c	ArO^-	2.73[e]
3b	$RCOO^-$	1.55[e]
	ArO^-	2.25[e]
3a	ArO^-	1.80[e]
1d	$RCOO^-$	0.41[f]
	ArO^-	1.75[f]
CH_3NO_2	RR′NH	0.73[b,g]
	ArO^-	(1.5)[b,c]
1b	$RCOO^-$	−0.60[f]
	ArO^-	0.50[f]
$C_6H_5CH_2NO_2$	$RCOO^-$	−0.59[b,g]
	ArO^-	(0.10)[b,c]
1a	$RCOO^-$	−1.10[f]
	ArO^-	0[f]

[a] In water, ref 1c. [b] $T = 20$ °C, ref 38. [c] Values in parentheses are estimated on the basis that log k_0 values for both $RCOO^-$ anions and secondary amines are generally lower than those for ArO^- ions by about 0.8 ± 0.2 log k unit.[1c] [d] $T = 20$ °C, ref 41b. [e] This work. [f] Ref 5b. [g] $T = 20$ °C, ref 41c.

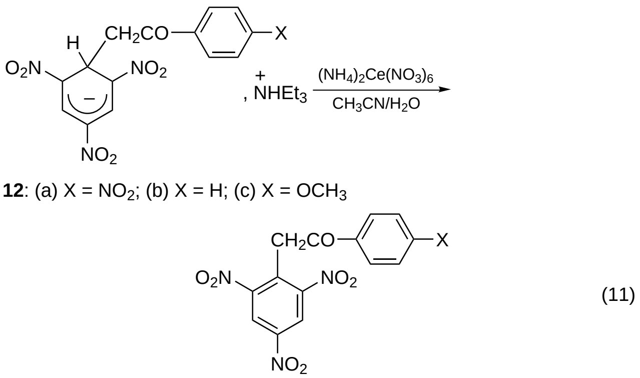
exocyclic carbon with only one aromatic rings; i.e., the conjugation is restricted to one picryl ring at a given time.[5b]

On the other hand, Table 6 shows that the log k_0 values for **3a**−**c** are much higher than those associated with the ionization of (2,4,4′-trinitrodiphenyl)methane (**1a**) and (2,2′,4,4′-tetranitrodiphenyl)methane (**1b**), two compounds which give rise to planar carbanions (**C-1a** and **C-1b**) with a much higher potentiality of delocalization of negative charge than **C-3a**−**c**. Also, the intrinsic reactivities of **3a**−−**c** are greater than those of nitroalkanes like nitromethane and phenylnitromethane. In these two latter compounds, the structural reorganization required to form the conjugate nitronate carbanions is reduced compared to that involved in the formation of **C-3a**−**c** but the concentration of charge onto the oxygen atoms of the adjacent NO_2 group is more favorable to hydrogen-bonding solvation. It is probably this factor which accounts for the lower log k_0 values for nitromethane and phenylnitromethane.[41c]

Experimental Section

Materials. Solvents were purified and solutions made up as described previously.[5] Buffers were purified commercial products.

Picrylacetophenone (**3b**) and the related *p*-nitro and *p*-methoxy derivatives **3a** and **3c** were prepared by oxidation of the σ-adducts **12a**−**c** according to eq 11.[18] These adducts were readily obtained as crystalline triethylammonium salts from the reaction of 1,3,5-trinitrobenzene with the appropriate acetophenone in the presence of triethylamine, as described previously.[18]



12: (a) X = NO_2; (b) X = H; (c) X = OCH_3

(11)

The oxidation of each of the three adducts **12a**−**c** was carried out as follows: 1 g of the appropriate triethylammonium salt was dissolved in 30 mL of a 2:1 (v/v) H_2O−CH_3CN mixture. To this stirred solution was added dropwise a solution of 2 equiv of ammonium cerium(IV) nitrate in 10 mL of water. The resulting solutions were allowed to stand for a few hours at room temperature (1 h 30 min for **3a**, 2 h 30 min for **3b**, and 24 h for **3c**). Then, removal of part of the solvent resulted in a precipitation of crude products which were collected by filtration and washed with water. Recrystallization in a pentane−ethyl acetate mixture (**3a**, **3b**) or a pentane−methanol mixture (**3c**) afforded analytical examples of **3a**, **3b**, and **3c** in 60%, 69.5%, and 40% yields, respectively.

3a: mp 180°C; mass spectrum $m/z = 377$ $(M + 1)^+$. Anal. Calcd for $C_{14}H_8N_4O_9$: C, 44.72; H, 2.14; N, 14.9. Found: C, 45.07; H, 1.83; N, 14.63.

3b: mp 135 °C; mass spectrum $m/z = 332$ $(M + 1)^+$. Anal. Calcd for $C_{14}H_9N_3O_7$: C, 50.8; H, 2.74; N, 12.69. Found: C, 51.43; H, 2.75; N, 12.55.

3c: mp 112°C; mass spectrum $m/z = 362$ $(M + 1)^+$. Anal. Calcd for $C_{15}H_{11}N_3O_8$: C, 49.86; H, 3.07; N, 11.64. Found: C, 49.97; H, 3.03; N, 11.61.

Measurements. Kinetic measurements were carried out with a Durrum stopped-flow spectrophotometer equipped with a thermostated cell compartment (25 °C ± 0.2). Some slow rates were measured with a conventional UV−vis Kontron-Uvikon spectrophotometer. All rates were reproducible to within ±5%. pH and pK_a determinations in the 50:50 (v/v) H_2O−Me_2SO mixture containing 0.5 M NMe_4Cl were carried out at 25 °C using the same procedures as those previously described.[5] A Tacussel Isis 20000 electronic pH meter was ued for this purpose. The autoprotolysis constant of this solvent mixture was known from previous studies: pK_s = 15.83 at 25 °C.[5]

^1H and ^{13}C NMR spectra were recorded on a Brucker AC300 spectrometer. Chemical shifts are reported in ppm (J values in Hz) with tetramethylsilane (Me_4Si) as the internal reference.

Mass spectra (EI, 70 eV) were obtained using a NERMAG R10-10C.

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Supporting Information Available: Observed first-order rate constants, k_{obsd}, for the ionization of picrylacetophenones **3a**−**c** in phenol and carboxylic acid buffer solutions (Table S1−S4) as well as in tetramethylammonium hydroxide and hydrochloric acid solutions (Tables S5 and S6) in 50:50 (v/v) H_2O−Me_2SO at 25 °C. Variation of the ratio of ionized to unionized picrylacetophenones **3a**−**c** as a function of pH, effect of the X substituent in the benzoyl moiety on the acidity of the picrylacetophenones **3a**−**c**, and Brönsted plots for the ionization of **3a** and **3c** by phenoxide ions in 50:50 (v/v) H_2O−Me_2SO at 25 °C (12 pages). This material is contained in 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.

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