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Proton Transfer from Carbon Acids to Carbanions. 2.[1] Reaction of Phenylnitromethane with Carbanions, Enolate, and Nitronate Ions in 90% Me_2SO–10% Water. Carbon to Carbon or Carbon to Oxygen Proton Transfer? Test of the Marcus Equation

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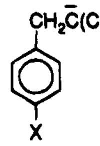
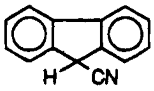
The kinetics of reactions of phenylnitromethane with the anions of 9-cyanofluorene, 4-nitrophenylacetonitrile, 1,3-indandione, Meldrum's acid, acetylacetone, and nitromethane (the "buffers") were measured by the stopped-flow technique. With the 1,3-indandionyl and 9-cyanofluorenyl anion, two kinetic processes [τ_1^{-1} and τ_2^{-1}] could be observed, while with the other buffer anions the τ_1^{-1} process was too fast to be measured and only the slow reaction [τ_2^{-1}] was accessible. The fast process refers to the reaction of the *aci*-form of phenylnitromethane with the buffer anion, which in the case of the 1,3-indandione buffer appears to proceed predominantly by an oxygen to oxygen proton transfer. The slow process corresponds to the deprotonation of the carbon of phenylnitromethane by the buffer anions. With the 1,3-indandione, Meldrum's acid, and nitromethane buffers, there is strong evidence that this deprotonation occurs mainly by carbon to carbon proton transfer, while with acetylacetone the reaction represents carbon to oxygen proton transfer. These conclusions are based on estimates of the intrinsic rate constants or intrinsic barriers of the various processes. Using identity barriers determined by the recently proposed "9-cyanofluorene method" (Bernasconi, C. F.; Ni, J. X. *J. Am. Chem. Soc.* **1993**, *115*, 5060), we have calculated the intrinsic barriers for the reactions of $PhCH_2NO_2$ with the anions of 9-cyanofluorene and 4-nitrophenylacetonitrile based on the Marcus equation. There is good agreement between the calculated and the experimental intrinsic barriers.

In a recent paper[1] we reported proton transfer rate constants for the reaction of substituted benzylmalononitrile anions (**1-X**$^-$) with various carbon acids (**2**–**6**) in


1-X$^-$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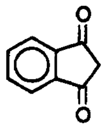
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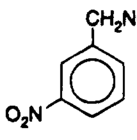
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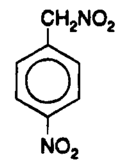
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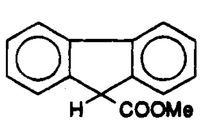
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90% Me_2SO–10% water. In contrast to water or more aqueous Me_2SO–water mixtures, in which proton transfer involving the solvent, lyonium ion, or lyate ion dominate the reaction, carbon to carbon proton transfer can easily be measured in 90% Me_2SO–10% water.

The results of these rate measurements allowed the calculation of intrinsic rate constants, k_o ($k_o = k$ when $K = 1$), or intrinsic barriers, $\Delta G^\ddagger_0$ ($\Delta G^\ddagger_0 = \Delta G^\ddagger$ when $\Delta G^\circ = 0$), for the proton transfer between **1-X**$^-$ and **2**–**6**. Note that we use the simplest definition of k_o and $\Delta G^\ddagger_0$, which differs from the Marcus[2] definition in that the work term for bringing the reactants together is included in $\Delta G^\ddagger_0$. We found log k_o to be an average of 1.77 log units lower ($\Delta G^\ddagger_0$ an average of 2.36 kcal/mol higher) than for the reactions of **2**–**6** with secondary cyclic amines (log k_o determined by extrapolation of two-point Brønsted plots for the reactions with piperidine and morpholine). This finding was shown to be consistent with the Marcus[2] eqs 1 and 2;[3]

$$\Delta G^\ddagger_0(CH/B^-) = \frac{1}{2}\{\Delta G^\ddagger_0(CH/C^-) + \Delta G^\ddagger_0(BH/B^-)\} \quad (1)$$

$$\Delta G^\ddagger_0(CH/A) = \frac{1}{2}\{\Delta G^\ddagger_0(CH/C^-) + \Delta G^\ddagger_0(AH^+/A)\} \quad (2)$$

$\Delta G^\ddagger_0(CH/B^-)$ refers to the intrinsic barrier of eq 3 (CH = **2**–**6**, B^- = **1-X**$^-$), $\Delta G^\ddagger_0(CH/A)$ to the intrinsic barrier of eq 4 (A = amine), while $\Delta G^\ddagger_0(CH/C^-)$, $\Delta G^\ddagger_0(BH/B^-)$ and $\Delta G^\ddagger_0(AH^+/A)$ are the intrinsic barriers of the identity reactions of eqs 5–7, respectively. By subtracting eq 2 from eq 1 one obtains

$$CH + B^- \rightleftharpoons C^- + BH \quad (3)$$

$$CH + A \rightleftharpoons C^- + AH^+ \quad (4)$$

$$CH + C^- \rightleftharpoons C^- + CH \quad (5)$$

$$BH + B^- \rightleftharpoons B^- + BH \quad (6)$$

$$AH^+ + A \rightleftharpoons A + AH^+ \quad (7)$$

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

[1] Part I: Bernasconi, C. F.; Ni, J. X. *J. Am. Chem. Soc.* **1993**, *115*, 5060.

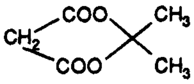
0022-3263/94/1959-4910$04.50/0

$$\Delta\Delta G_0^{\ddagger} = \Delta G_0^{\ddagger}(\mathrm{CH/B^-}) - \Delta G_0^{\ddagger}(\mathrm{CH/A}) = \frac{1}{2}\{\Delta G_0^{\ddagger}(\mathrm{BH/B^-}) - \Delta G_0^{\ddagger}(\mathrm{AH^+/A})\} \quad (8)$$

Since proton transfer from nitrogen to nitrogen is generally much faster than carbon to carbon proton transfer (e.g., $\Delta G_0^{\ddagger}(\mathrm{BH/B^-}) \gg \Delta G_0^{\ddagger}(\mathrm{AH^+/A})$, with $\mathrm{BH/B^-}$ referring to **1-X**/**1-X**$^-$), it follows that $\Delta G_0^{\ddagger}(\mathrm{CH/B^-}) \gg \Delta G_0^{\ddagger}(\mathrm{CH/A})$. Our experimental results confirm this expectation and indicate that $\Delta\Delta G_0^{\ddagger} = 2.36$ kcal/mol (eq 8), suggesting that $\Delta G_0^{\ddagger}(\mathrm{BH/B^-})$ for BH = **1-X** is 4.72 kcal/mol higher than $\Delta G_0^{\ddagger}(\mathrm{AH^+/A})$.

These results were exploited to estimate intrinsic barriers of identity reactions as follows. One approach was to assume $\Delta G_0^{\ddagger}(\mathrm{AH^+/A}) = 6.8$ kcal/mol on the basis of Grunwald's data for the $(\mathrm{CH_3})_2\mathrm{NH_2}^+/(\mathrm{CH_3})_2\mathrm{NH}$ system.[4] This value for $\Delta G_0^{\ddagger}(\mathrm{AH^+/A})$ was used to calculate $\Delta G_0^{\ddagger}(\mathrm{BH/B^-})$ from eq 8 while $\Delta G_0^{\ddagger}(\mathrm{BH/B^-})$ obtained from this procedure was used to calculate $\Delta G_0^{\ddagger}(\mathrm{CH/B^-})$ for CH = **2**–**6** from eq 1. The various $\Delta G_0^{\ddagger}$ values are reported in Table 1 under "amine method." An alternative set was based on an estimate of 13.05 kcal/mol for $\Delta G_0^{\ddagger}(\mathrm{CH/C^-})$ for CH = **2**. This estimate was deduced from rate data for the reactions of **2** with the anion of 9-carbomethoxyfluorene (**7**)[5] and comparisons of rates for the reactions of **2** and **7** with amines. Using $\Delta G_0^{\ddagger}(\mathrm{CH/C^-})$ for CH = **2** in eq 1 allowed the calculation of $\Delta G_0^{\ddagger}(\mathrm{BH/B^-})$, which became the basis for calculating $\Delta G_0^{\ddagger}(\mathrm{CH/C^-})$ for CH = **3**–**6** from eq 1 and $\Delta G_0^{\ddagger}(\mathrm{AH^+/A})$ from eq 2. This second set of $\Delta G_0^{\ddagger}$ values is included in Table 1 under "9-cyanofluorene method."

There is a substantial difference in the two sets of calculated intrinsic barriers of identity reactions. Even though the second set was preferred,[1] no definite conclusions as to the validity of any one set could be reached. The present paper addresses this issue. We have studied the kinetics of the reaction of phenylnitromethane with the anions of 9-cyanofluorene (**2**), 1,3-indandione (**3**), 4-nitrophenylacetonitrile (**4**), Meldrum's acid (**8**), acetylacetone (**9**), and nitromethane (**10**), and obtained approximate intrinsic barriers for these reactions. The results of the reactions of phenylnitromethane with **2**$^-$ and **4**$^-$ will be shown to support the calculations of identity barriers by the "9-cyanofluorene method."



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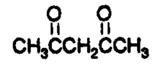

$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3}$

9

$\mathrm{CH_3NO_2}$

10

Another interesting question that arises for the reactions of phenylnitromethane with the enolate ions **3**$^-$, **8**$^-$, and **9**$^-$ and the nitronate ion **10**$^-$ is whether the phenylnitromethane proton is abstracted by the oxygen or the carbon of these bases. It will be shown that with **3**$^-$, **8**$^-$, and **10**$^-$ carbon to carbon proton transfer and with **9**$^-$ carbon to oxygen proton transfer is dominant.

Table 1. Intrinsic Rate Constants and Intrinsic Barriers of Identity Reactions According to Equations 5–7 in 90% Me$_2$SO–10% Water (v/v) at 20 °C, μ = 0.06 M[a]

	amine method		9-cyanofluorene method	
acid	log k_o	$\Delta G_o^{\ddagger}$, kcal/mol	log k_o	$\Delta G_o^{\ddagger}$, kcal/mol
$\mathrm{R_2NH_2^+}$	7.70	6.80[b]	5.76	9.37[b]
benzylmalononitriles (**1-X**)	4.16	11.52[c]	2.40	13.87[c]
9-cyanofluorene (**2**)	1.24	15.40[d]	3.00	13.05[d]
1,3-indandione (**3**)	0.25	16.72[d]	2.02	14.37[d]
4-nitrophenylacetonitrile (**4**)	−0.42	17.62[d]	1.42	15.17[d]
(3-nitrophenyl)nitromethane (**5**)	−3.50	21.74[d]	−1.74	19.39[d]
(4-nitrophenyl)nitromethane (**6**)	−3.67	21.96[d]	−1.91	19.61[d]
phenylnitromethane (**7**)	−4.18	22.64[d]	−2.33	20.17[d]

[a] Reference 1. [b] $\Delta G_0^{\ddagger}(\mathrm{AH^+/A})$. [c] $\Delta G_0^{\ddagger}(\mathrm{BH/B^-})$. [d] $\Delta G_0^{\ddagger}(\mathrm{CH/C^-})$.

Results

General Features. All kinetic experiments were carried out in 90% Me$_2$SO–10% water (v/v) at 20 °C. The ionic strength was maintained at 0.06 M with KCl. The reactions were run under pseudo-first-order conditions with phenylnitromethane (SH) or its anion (S$^-$) as the "substrate" and the other carbon acids/carbanions as the "buffer." In order to avoid confusion with the symbols used in our previous study (BH = **1-X**, which was used as the buffer; CH for all other carbon acids that were used as substrates), we shall keep the symbol CH for **2**–**4** and **8**–**10**, even though in the present study they are the buffers, and we shall consistently use SH for phenylnitromethane.

Two kinds of kinetic situations were encountered. The first pertains to buffers that do not tautomerize, such as **2** and **4**. The reaction scheme can be described by eq 9.

$$\underset{\mathrm{SH}}{\mathrm{PhCH_2NO_2}} \xrightleftharpoons[k_{-2}^{\mathrm{H}}a_{\mathrm{H^+}} + k_{-2}^{\mathrm{H_2O}} + k_{-2}^{\mathrm{CH}}[\mathrm{CH}]]{k_2^{\mathrm{H_2O}} + k_2^{\mathrm{OH}}a_{\mathrm{OH^-}} + k_2^{\mathrm{C}}[\mathrm{C^-}]}$$

$$\underset{\mathrm{S^-}}{\mathrm{PhCH{=}NO_2^-}} \xrightleftharpoons[k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}a_{\mathrm{OH^-}} + k_1^{\mathrm{C}}[\mathrm{C^-}]]{k_{-1}^{\mathrm{H}}a_{\mathrm{H^+}} + k_{-1}^{\mathrm{H_2O}} + k_{-1}^{\mathrm{CH}}[\mathrm{CH}]} \underset{\mathrm{HS}}{\mathrm{PhCH{=}NO_2H}} \quad (9)$$

It is characterized by two kinetic processes. The first refers to the S$^-$ ⇌ HS (note the distinction between SH and HS) equilibrium, with the reciprocal relaxation time, τ_1^{-1}, for equilibration being given by eq 10.[6] The second

$$\tau_1^{-1} = k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}a_{\mathrm{OH^-}} + k_{-1}^{\mathrm{H}}a_{\mathrm{H^+}} + k_{-1}^{\mathrm{H_2O}} + k_1^{\mathrm{C}}[\mathrm{C^-}] + k_{-1}^{\mathrm{CH}}[\mathrm{CH}] \quad (10)$$

kinetic process refers to the SH ⇌ S$^-$ reaction, with the S$^-$ ⇌ HS process acting as a fast preequilibrium and τ_2^{-1} being given by eq 11.[6] K_a^{HS} is the acid dissociation

$$\tau_2^{-1} = k_2^{\mathrm{H_2O}} + k_2^{\mathrm{OH}}a_{\mathrm{OH^-}} + (k_{-2}^{\mathrm{H}}a_{\mathrm{H^+}} + k_{-2}^{\mathrm{H_2O}})\frac{K_a^{\mathrm{HS}}}{K_a^{\mathrm{HS}} + a_{\mathrm{H^+}}} + k_2^{\mathrm{C}}[\mathrm{C^-}] + k_{-2}^{\mathrm{CH}}[\mathrm{CH}]\frac{K_a^{\mathrm{HS}}}{K_a^{\mathrm{HS}} + a_{\mathrm{H^+}}} \quad (11)$$

constant of the *aci*-form of phenylnitromethane, HS; $\mathrm{p}K_a^{\mathrm{HS}} = 7.73$.[8]

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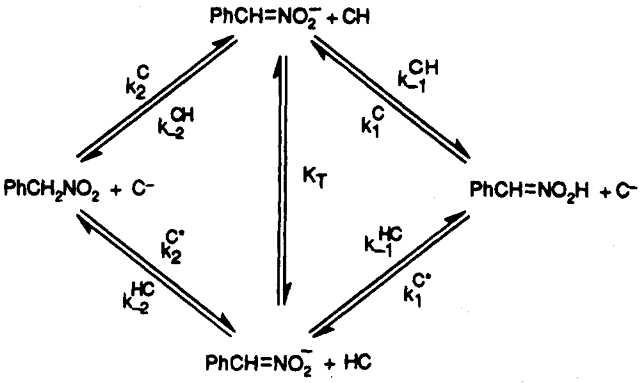
(2) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (c) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249.

(3) Again, the work term is included in the various $\Delta G_0^{\ddagger}$ values. For the purposes of the present study, this simplification is inconsequential. For a more extensive discussion of this issue see ref 1.

(4) (a) Grunwald, E.; Ku, A. Y. *J. Am. Chem. Soc.* **1968**, *90*, 29. (b) Grunwald, E.; Ralph, E. K., III *Acc. Chem. Res.* **1971**, *4*, 107.

(5) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1987**, *109*, 7115.

Scheme 1



When the reactions are run by mixing SH with a basic solution of the CH/C$^-$ buffer, the first process cannot be seen, and if pH $\gg$ pK_a^{HS}, as is the case for the reaction with **4**, eq 11 for τ_2^{-1} simplifies to

$$\tau_2^{-1} = k_2^{H_2O} + k_2^{OH}a_{OH^-} + k^{H}_{-2}a_{H^+} + k_{-2}^{H_2O} + k_2^C[C^-] + k_{-2}^{CH}[CH] \quad (12)$$

On the other hand, when the reaction is initiated by mixing a strongly basic solution of S$^-$ with a less basic (or slightly acidic) solution of the CH/C$^-$ buffer, the first process is, in principle, visible. Whether τ_1^{-1} can be measured or not depends on whether or not it falls within the time range of the stopped-flow technique. With CH = **2**, τ_1^{-1} was measurable, but not with CH = **4**.

The second situation prevails when the buffers tautomerize into enols or nitronic acids, as is the case with **3** and **8**–**10**. The scheme of eq 9 is still valid but the buffer terms change their meaning as shown in eqs 13–16, with HC being the enol or *aci*-form, respectively, of

$$k_1^C[C^-] \text{ becomes } (k_1^C + k_1^{C*})[C^-] \quad (13)$$

$$k_{-1}^{CH}[CH] \text{ becomes } k_{-1}^{CH}[CH] + k_{-1}^{HC}[HC] = (k_{-1}^{CH} + k_{-1}^{HC}K_T)[CH] \quad (14)$$

$$k_2^C[C^-] \text{ becomes } (k_2^C + k_2^{C*})[C^-] \quad (15)$$

$$k_{-2}^{CH}[CH] \text{ becomes } k_{-2}^{CH}[CH] + k_{-2}^{HC}[HC] = (k_{-2}^{CH} + k_{-2}^{HC}K_T)[CH] \quad (16)$$

the buffers and K_T being its tautomerization equilibrium constants. The new rate constants refer to the reactions shown in Scheme 1.

Just as before, there are two potentially visible kinetic processes, with the relaxation times given by eqs 10 and 11, respectively, but with the substitutions according to eqs 13–16; the tautomerization of the buffer adds a third kinetic process, but this reaction is too fast to be seen by the stopped-flow method.

The kinetic experiments were run with substrate concentrations in the range of 1–5 × 10^{-5} M and total buffer concentrations in the range of 3 × 10^{-4}–5 × 10^{-3} M. The τ_1^{-1} and τ_2^{-1} values were determined spectrophotometrically from plots of ln(ΔOD) vs time, with ΔOD being the changes in optical density induced by the reaction. Details are given in the Experimental Section. The range of buffer concentrations was dictated by the need to maintain pseudo-first-order conditions, on the one hand, and the onset of buffer association at high concentrations, on the other. This buffer association, which we attribute to the formation of homoconjugate pairs, CH·C$^-$, manifests itself as downward curvature in the buffer plots at concentrations above 5 × 10^{-3}–10^{-2} M. In the following sections we report our results in some detail; the raw data (τ_1^{-1} and τ_2^{-1} values) are summarized elsewhere.[9]

Reaction with 4-Nitrophenylacetonitrile (4) Buffer. Only the τ_2^{-1} process was measurable. τ_2^{-1} was determined as a function of buffer base concentration at pH 12.03, 12.33, and 12.93. A representative plot is shown in Figure S1 of the supplementary material.[10] Under these conditions eq 12 simplifies further to

$$\tau_2^{-1} \approx k_2^{H_2O} + k_2^{OH}a_{OH^-} + k_2^C[C^-] \quad (17)$$

This is confirmed by the fact that the slopes of the plots of τ_2^{-1} vs [C$^-$] are, within experimental error, independent of pH (Table 2); dominance of the forward reaction is expected on the basis of the pK_a^{SH} of phenylnitromethane (10.68).

Reaction with 9-Cyanofluorene (2) Buffer. Due to the low pK_a of **2** (pK_a^{CH} = 8.01) the reactions were conducted by mixing the phenylnitromethane anion with the buffer solutions at pH 7.17, 7.31, 7.53, 8.01, and 8.31. Both τ_1^{-1} and τ_2^{-1} could be determined as functions of buffer concentration. A representative buffer plot for τ_1^{-1} is shown in Figure S2.[10] The slopes of the plots of τ_1^{-1} vs [CH] are given by eq 18, those of τ_2^{-1} vs [CH] by eq 19; note that the k_2^C[C$^-$] term is negligible at pH 7.17–8.31.

$$\text{slope}_1 = k_1^C K_a^{CH}/a_{H^+} + k_{-1}^{CH} \quad (18)$$

$$\text{slope}_2 = k_{-2}^{CH}\frac{K_a^{HS}}{K_a^{HS} + a_{H^+}} \quad (19)$$

From eq 18 we obtain k_{-1}^{CH} = (8.09 ± 0.15) × 10^4 M^{-1} s^{-1} and $k_1^C K_a^{CH}$ = (1.58 ± 0.16) × 10^{-3} s^{-1} from which k_1^C = (1.62 ± 0.16) × 10^5 M^{-1} s^{-1} can be calculated. The ratio k_1^C/k_{-1}^{CH} (2.00) is in excellent agreement with K_a^{HS}/K_a^{CH} = 1.91 calculated from the respective known pK_a values (Table 4), showing excellent internal consistency and confirming our interpretation of the τ_1^{-1} process being due to the reversible deprotonation of the *aci*-phenylnitromethane.

Inverting eq 19 leads to eq 20 and yields k_{-2}^{CH} = 19.6 ± 1.8 M^{-1} s^{-1} and k_{-2}^{CH} = 24.6 ± 2.3 M^{-1} s^{-1} from the

$$\text{slope}_2^{-1} = 1/k_{-2}^{CH} + a_{H^+}/k_{-2}^{CH}K_a^{HS} \quad (20)$$

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[6] The reciprocal relaxation time for the equilibration of a reversible reaction run under pseudo-first-order conditions is synonymous with the pseudo-first-order rate constant for equilibration. Hence it is equal to the sum of all pseudo-first-order rate constants in the forward and reverse directions. If a step of the reaction under study is coupled to a fast preequilibrium, the pseudo-first-order rate constants of that step are multiplied by a factor that reflects the position of that preequilibrium.[7]

[7] (a) Bernasconi, C. F. *Relaxation Kinetics*, Academic Press: New York, 1976; Chapters 2 and 3. (b) Bernasconi, C. F. In *Investigation of Rates and Mechanisms of Reactions*, Bernasconi, C. F., Ed., Wiley-Interscience: New York, 1986; Part 1, p 425.

[8] Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S., Ni, J. X. *J. Org. Chem.* **1988**, *53*, 3342.

[9] Ni, J. X. Ph.D. Thesis, University of California, Santa Cruz, 1990.

[10] See paragraph concerning supplementary material at the end of this paper.

Table 2. Slopes of Plots of τ_1^{-1} and τ_2^{-1} vs Buffer Concentration in 90% Me_2SO–10% Water (v/v) at 20 °C, μ = 0.06 M

	slope, $M^{-1}\ s^{-1}$	
pH	τ_1^{-1}	τ_2^{-1}
	9-Cyanofluorene (**2**)[a]	
7.17	(1.05 ± 0.02) × 10^5	5.08 ± 0.12
7.31	(1.13 ± 0.04) × 10^5	6.17 ± 0.36
7.53	(1.35 ± 0.03) × 10^5	8.79 ± 0.35
8.01	(2.39 ± 0.08) × 10^5	13.6 ± 0.2
8.31	(4.00) ± 0.12) × 10^5	16.7 ± 0.8
	1,3-Indandione (**3**)[a]	
6.98	(9.25 ± 0.28) × 10^4	
7.12	(1.00 ± 0.04) × 10^5	
7.34	(1.16 ± 0.04) × 10^5	
7.52	(1.32 ± 0.05) × 10^5	(3.08 ± 0.14) × 10^1
7.82	(1.80 ± 0.12) × 10^5	(5.46 ± 0.15) × 10^1
8.12		(9.22 ± 0.07) × 10^1
8.42		(1.38 ± 0.04) × 10^2
	4-Nitrophenylacetonitrile (**4**)[b]	
12.04		2.13 ± 0.06
12.33		2.17 ± 0.07
12.93		2.20 ± 0.11
	Meldrum's Acid (**8**)[a]	
5.34		(4.13 ± 0.15) × 10^{-1}
5.70		(9.95 ± 0.20) × 10^{-1}
6.18		2.57 ± 0.08
6.48		5.47 ± 0.15
6.78		11.6 ± 0.6
	Acetylacetone (**9**)[b]	
11.16		76.5 ± 1.5
11.76		70.2 ± 2.0
12.06		68.1 ± 2.5
	CH_3NO_2 (**10**)[b]	
13.50		11.1 ± 0.6
13.80		9.4 ± 0.6
14.32		10.9 ± 0.6

[a] τ_1^{-1} and τ_2^{-1} vs [CH]. [b] τ_1^{-1} and τ_2^{-1} vs [C⁻].

intercept and slope, respectively, of the plot according to eq 20. We shall adopt the average k_{-2}^{CH} = 22.1 $M^{-1}\ s^{-1}$ from which $k_2^{C} = k_{-2}^{CH}K_a^{SH}/K_a^{CH}$ = 4.72 × 10^{-2} $M^{-1}\ s^{-1}$ is calculated.

Reaction with 1,3-Indandione (3) Buffer. Just as with the 9-cyanofluorene buffer, the equilibrium was approached from the PhCH=NO_2^- side and both τ_1^{-1} (at pH 6.98, 7.12, 7.34, 7.52 and 7.82) and τ_2^{-1} (at pH 7.12, 7.52, 7.82, 8.12, and 8.42) could be measured.

The slopes of the plots of τ_1^{-1} and τ_2^{-1} vs [CH] conform to eqs 21 and 22, respectively. From slope₁ one calculates

$$\text{slope}_1 = (k_1^{C} + k_1^{C*})K_a^{CH}/a_{H^+} + k_{-1}^{CH} + k_{-1}^{HC}K_T \quad (21)$$

$$\text{slope}_2 = (k_{-2}^{CH} + k_{-2}^{HC}K_T)\frac{K_a^{HS}}{K_a^{HS} + a_{H^+}} \quad (22)$$

$k_1^{C} + k_1^{C}*$ = (1.01 ± 0.1) × 10^5 $M^{-1}\ s^{-1}$ and $k_{-1}^{CH} + k_{-1}^{HC}K_T$ = (8.02 + 0.15) × 10^4 $M^{-1}\ s^{-1}$; the ratio $(k_1^{C} + k_1^{C}*)/(k_{-1}^{CH} + k_{-1}^{HC}K_T)$ = 1.26 compares very favorably with K_a^{HS}/K_a^{CH}= 1.23, calculated from the known pK_a^{HS} and pK_a^{CH} values, again confirming that the reaction refers to the reversible deprotonation of the *aci*-phenylnitromethane.

From an inversion plot of slope_2^{-1} *vs* a_{H^+}, we obtain $k_{-2}^{CH} + k_{-2}^{HC}K_T$ = 42.4 ± 15.0 $M^{-1}\ s^{-1}$ (intercept of inversion plot) and $k_{-2}^{CH} + k_{-2}^{HC}K_T$ = 50.1 ± 4.0 $M^{-1}\ s^{-1}$ (slope of inversion plot), respectively. The former value is rather uncertain and hence we shall adopt the latter value. It yields $k_2^{C} + k_2^{C}* = (k_{-2}^{CH} + k_{-2}^{HC}K_T)K_a^{SH}/K_a^{CH}$ = 6.91 × 10^{-2} $M^{-1}\ s^{-1}$.

Table 3. Intercepts of Plots of τ_2^{-1} vs [CH] or [C⁻] in 90% Me_2SO–10% Water (v/v) at 20 °C, μ = 0.06 M

		int₂, s^{-1}	
buffer	pH	obsd	calc[a]
Meldrum's acid	5.35	(8.6 ± 0.8) × 10^{-4}	8.83 × 10^{-4}
	5.70	(1.1 ± 0.1) × 10^{-3}	8.79 × 10^{-4}
	6.18	(1.8 ± 0.3) × 10^{-3}	8.60 × 10^{-4}
9-cyanofluorene	7.17	(7.8 ± 1.5) × 10^{-4}	6.95 × 10^{-4}
4-nitrophenylacetonitrile	12.93	(8.1 ± 0.4) × 10^{-4}	
CH_3NO_2	13.50	(7.8 ± 2.5) × 10^{-3}	
	13.80	(1.7 ± 0.5) × 10^{-2}	
	14.32	(4.0 ± 0.5) × 10^{-2}	

[a] See text.

Reaction with Meldrum's Acid (8) Buffer. The reactions were run at pH 5.34, 5.70, 6.18, 6.48, and 6.78. τ_1^{-1} was too fast for the stopped-flow method. The slopes of plots of τ_2^{-1} vs [CH] are given by eq 22, which, due to the low pH, can be approximated by slope₂ = $(k_{-2}^{CH} + k_{-2}^{HC}K_T)K_a^{SH}/a_{H^+}$. The slope of a plot of slope₂ vs $a^{-1}{}_{H+}$ affords $k_{-2}^{CH} + k_{-2}^{HC}K_T$ = (1.02 ± 0.05) × 10^2 $M^{-1}\ s^{-1}$ from which $k_2^{C} + k_2^{C}*$ = 3.24 × 10^{-3} $M^{-1}\ s^{-1}$ is calculated.

Reaction with Acetylacetone (9) and Nitromethane (10) Buffers. The reactions were conducted by mixing phenylnitromethane with a basic solution of the buffer, specifically at pH 11.16, 11.76, and 12.06 with acetylacetone and at pH 13.50, 13.80 and 14.32 with nitromethane. Only τ_2^{-1} could be observed. The slopes of the buffer plots (τ_2^{-1} vs [C⁻]) are given by eq 23 which

$$\text{slope}_2 = k_2^{C} + k_2^{C*} + (k_{-2}^{CH} + k_{-2}^{HC}K_T)a_{H^+}/K_a^{CH} \quad (23)$$

simplifies to slope₂ = $k_2^{C} + k_2^{C}*$ for the nitromethane reaction. The data yield $k_2^{C} + k_2^{C}*$ = 10.5 ± 0.5 $M^{-1}\ s^{-1}$ (average of slopes) for nitromethane, and $k_2^{C} + k_2^{C}*$ = 65.1 ± 8.0 $M^{-1}\ s^{-1}$ (slopes extrapolated to a_{H^+} = 0) for acetylacetone.

Intercepts of Buffer Plots. Most buffer plots had measurable, albeit sometimes rather small, intercepts which made some of them quite uncertain. Additional uncertainty was introduced when conducting some of the reactions under less than ideal pseudo-first-order conditions (ratios of less than 10:1) at the low end of the buffer concentration range. These conditions were necessary to enhance the absorbance change during the reaction. We therefore only report those intercepts which we deem to be reasonably certain. They are summarized in Table 3; they all refer to the τ_2^{-1} process.

According to eq 12 these intercepts are given by

$$\text{int}_2 = k_2^{H_2O} + k_2^{OH}a_{OH^-} + (k_{-2}^{H_2O} + k_{-2}^{H}a_{H^+})\frac{K_a^{HS}}{K_a^{HS} + a_{H^+}} \quad (24)$$

The points at pH 12.93 to 14.32 can be fit to int₂ = $k_2^{OH}a_{OH^-}$; the value of $k_2^{H_2O}$ = 9.96 × 10^{-7} s^{-1}, determined previously,[8] is much too small to contribute to int₂ in this pH range. The results yield k_2^{OH} = 2.1 ± 0.3 × 10^6 M^{-1} s^{-1} from which $k_{-2}^{H_2O} = k_2^{OH}K_w/K_a^{SH}$ = 9.06 × 10^{-6} s^{-1} is obtained. This $k_{-2}^{H_2O}$ is seen to be much smaller than the intercepts in the pH range 5.34–7.17, indicating that in this pH range int₂ is dominated by the $k_{-2}^{H}a_{H^+}K_a^{HS}/(K_a^{HS} + a_{H^+})$ term. If int₂ is calculated based on k_{-2}^{H} = 4.77 ×

Table 4. Rate Constants, pK_a Values, and Intrinsic Rate Constants for the Reversible Deprotonation of *aci*-Phenylnitromethane (HS) by 9-Cyanofluorenyl and 1,3-Indandionyl Anions (τ_1^{-1} Process)[a]

buffer	pK_a^{CH}	pK_a^{HC}	K_T	k_1^C or $k_1^C + k_1^{C*}$, M^{-1} s^{-1}	k_{-1}^{CH} or $k_{-1}^{CH} + k_{-1}^{HC}K_T$, M^{-1} s^{-1}	pK_a^{CH} − pK_a^{HS}	$\log(k_1^C)_o$	pK_a^{HC} − pK_a^{HS}	$\log(k_1^{C*})_o$
9-cyanofluorene (**2**)	8.01[b]			1.62×10^5 [c]	8.09×10^4 [c]	0.82	5.1		
1,3-indandione (**3**)	7.82[d]	5.53[d]	5.13×10^{-3}	1.01×10^5 [e]	8.02×10^4 [e]	0.09	5.0	−2.20	7.2

[a] pK_a^{HS} = 7.73. [b] Reference 5. [c] k_1^C, k_{-1}^{CH}. [d] Reference 11. [e] $k_1^C + k_1^{C*}$, $k_{-1}^{CH} + k_{-1}^{HC}K_T$.

Table 5. Rate Constants, pK_a Values, and Intrinsic Rate Constants for the Reversible Deprotonation of Phenylnitromethane (SH) by Various Carbanions (τ_2^{-1} Process)[a]

buffer	pK_a^{CH}	pK_a^{HC}	K_T	k_2^C or $k_2^C + k_2^{C*}$, M^{-1} s^{-1}	k_{-2}^{CH} or $k_{-2}^{CH} + k_{-2}^{HC}K_T$, M^{-1} s^{-1}	pK_a^{CH} − pK_a^{SH}	$\log(k_2^C)_o$	pK_a^{HC} − pK_a^{SH}	$\log(k_2^{C*})_o$
9-cyanofluorene (**2**)	8.01[f]			4.72×10^{-2} [b]	22.1[b]	−2.67	0.0 ± 0.5		
4-$NO_2C_6H_4CH_2CN$ (**4**)	12.03[g]			2.21[b]	9.86×10^{-2} [b]	2.35	−0.3 ± 0.5		
1,3-indandione (**3**)	7.82[h]	5.53[h]	5.23×10^{-3}	6.91×10^{-2} [c]	50.1[c]	−2.86	0.3 ± 0.6[d]	−5.15	2.7[e]
Meldrum's acid (**8**)	6.18[i]	<4.18[i]	$<10^{-2}$	3.24×10^{-3} [c]	1.02×10^2 [c]	−4.50	−0.2 ± 0.9[d]	< −7.15	>2.9[e]
acetylacetone (**9**)	11.10[j]	11.16[j]	1.15	65.9[c]	25.1[c]	0.42	1.6 ± 0.1[d]	0.48	1.5[e]
CH_3NO_2 (**10**)	14.80[k]	8.65[k]	7.08×10^{-7}	10.5[c]	7.95×10^{-4} [c]	4.12	−1.0 ± 0.8[d]	−2.03	2.5[e]

[a] pK_a^{SH} = 10.68. [b] k_2^C and k_{-2}^{CH}. [c] $k_2^C + k_2^{C*}$, $k_{-2}^{CH} + k_{-2}^{HC}k_T$. [d] Calculated assuming $k_2^C \gg k_2^{C*}$, $k_{-2}^{CH} \gg k_{-2}^{HC}K_T$. [e] Calculated assuming $k_2^{C*} \gg k_2^C$, $k_{-2}^{HC}K_T \gg k_{-2}^{CH}$. [f] Reference 5. [g] This work. [h] Reference 11. [i] Bernasconi, C. F.; Oliphant, N., unpublished results. [j] Reference 13. [k] Reference 8.

10^4 M^{-1} s^{-1} and pK_a^{HS} = 7.73 determined previously,[8] the values under the heading int$_2$ calc in Table 3 are obtained. With one exception (pH 6.18), the agreement between observed and calculated intercepts is excellent.

Discussion

The rate constants for the reactions of phenylnitromethane and its anion with the various buffers are summarized in Tables 4 (τ_1^{-1} process) and 5 (τ_2^{-1} process). The tables also report log k_o values, with k_o being the intrinsic rate constant defined as the rate constant that pertains when ΔpK = 0. Since no Brønsted plots are available which could serve to determine the various intrinsic rate constants through suitable interpolation or extrapolation, the k_o values had to be estimated as detailed below.

Estimate of $\log(k_1^C)_o$. $(k_1^C)_o$ is the intrinsic rate constant for proton transfer between the CH form of the buffer and the *aci*-form of phenylnitromethane, i.e., $(k_1^C)_o = k_1^C = k_{-1}^{CH}$ when pK_a^{CH} − pK_a^{HS} = 0. Since an *aci*-nitro compound is structurally quite similar to a carboxylic acid, and the value of pK_a^{HS} = 7.73 is within the range of pK_a's of typical carboxylic acids in 90% Me_2SO–10% water (pK_a = 9.53 for acetic acid, 6.84 for chloroacetic acid),[11] it is reasonable to assume that the Brønsted β values for the deprotonation of 9-cyanofluorene or 1,3-indandione by the nitro group of a series of phenylnitromethane anions would be similar to the β value generated by a series of carboxylate ions. For the deprotonation of 1,3-indandione by carboxylate ions, β = 0.74;[11] for 9-cyanofluorene it is unknown. In view of the fact that the β value for the deprotonation of 1,3-indandione[11] and 9-cyanofluorene[5] by primary aliphatic amines are quite similar to one another, it is reasonable to assume that β values for the deprotonation of these two carbon acids by carboxylate ions are also similar. Hence $\log(k_1^C)_o$ for both the 9-cyanofluorene and 1,3-indandione reactions (Table 4) were estimated assuming a β = 0.74. Incidentally, since ΔpK = pK_a^{CH} − pK_a^{HS} is very close to zero for the reaction of PhCH=NOH with both buffers, any error in the assumed β value would be inconsequential as far as the estimated $\log(k_1^C)_o$ is concerned.

Estimate of $\log(k_1^{C*})_o$. $(k_1^{C*})_o$ refers to the proton transfer between the enol form of the buffer and the *aci*-form of phenylnitromethane, i.e., $(k_1^{C*})_o = k_1^{C*} = k_{-1}^{HC}$ when pK_a^{HC} − pK_a^{HS} = 0. In the only example for which we were able to determine $\log(k_1^{C*})_o$, the reaction of 1,3-indandionyl anion with *aci*-phenylnitromethane, a $\beta \approx 1.0$ may be assumed in the thermodynamically disfavored direction (k_1^{C*}), or $\alpha \approx 0$ in the favorable direction (k_{-1}^{HC}).[12] The estimate for $(k_1^{C*})_o$ given in Table 4 is based on β = 1.0.

Estimate of $\log(k_2^C)_o$. $(k_2^C)_o$ refers to carbon to carbon proton transfer from CH to the carbon of phenylnitromethane anion, i.e., $(k_2^C)_o = k_2^C = k_{-2}^{CH}$ when pK_a^{CH} − pK_a^{SH} = 0. In the absence of experimentally determined relevant β values we shall, somewhat arbitrarily, assume β = 0.5 in all cases. This is the same β value that was observed in the reactions of **2**–**6** with a series of substituted benzylmalononitrile anions (**1-X**$^-$).[1] The potential error in $(k_2^C)_o$ that may arise if the assumed β value is erroneous is given by $|\Delta\beta(\text{p}K_a^{CH} - \text{p}K_a^{SH})|$ with Δβ being the difference between the true β value and 0.5. The uncertainties associated with the $\log(k_2^C)_o$ values reported in Table 5 were calculated by assuming a maximum Δβ of ±0.2.

Estimate of $\log(k_2^{C*})_o$. $(k_2^{C*})_o$ refers to the deprotonation of phenylnitromethane by the oxygen of the enolate ion (or $CH_2{=}NO_2^-$) of the buffers, i.e., $(k_2^{C*})_o = k_2^{C*} = k_{-2}^{HC}$ when pK_a^{HC} − pK_a^{SH} = 0. In the case of 1,3-indandione, Meldrum's acid, and nitromethane, the pK_a^{HC} values are in the same range as those for carboxylic acids, and hence we have calculated our $(k_2^{C*})_o$ values based on the β value (0.75) that was determined for the deprotonation of phenylnitromethane by carboxylate ions.[8] With acetylacetone, whose pK_a^{HC} = 11.16 is above the range for carboxylic acid, a β = 0.6 has been assumed, reflecting the tendency for β in such reactions to decrease at high pK_a values of the buffer.[13]

Interpretation of Intrinsic Rate Constants. A. $\log(k_1^C)_o$ and $\log(k_1^{C*})_o$. The $(k_1^C)_o$ values for the reaction of *aci*-phenylnitromethane with the 9-cyanofluorenyl ion, **2**$^-$, is estimated to be 5.11 (Table 4). Due to the strong structural similarity between the *aci*-form of a

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(11) Bernasconi, C. F.; Paschalis, P. *J. Am. Chem. Soc.* **1986**, *108*, 2969.

(12) Eigen, M. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 1.

nitro compound and a carboxylic acid, one expects $\log(k_1^{\mathrm{C}})_{\mathrm{o}}$ for our reaction to be similar to $\log k_{\mathrm{o}}$ for the reaction of **2**⁻ with carboxylic acids. The rates of the reaction of **2**⁻ with carboxylic acids are too fast to be measured in the stopped-flow apparatus, but $\log k_{\mathrm{o}}$ for such reactions may be estimated based on $\log k_{\mathrm{o}} = 3.57$ for the reaction of **2** with primary aliphatic amines.[8] For example, $\log k_{\mathrm{o}}$ for the reaction of 1,3-indandione (**3**) with carboxylate ions in 90% $\mathrm{Me_2SO}$−10% water (v/v) is 1.56 log units higher than $\log k_{\mathrm{o}}$ for the reaction of **3** with primary aliphatic amines,[11] and $\log k_{\mathrm{o}}$ for the reaction of phenylnitromethane with carboxylate ions is 0.91 log units higher than for the corresponding reaction with primary aliphatic amines.[8] If we assume a similar difference between $\log k_{\mathrm{o}}$ for amines and carboxylate ions in the reaction with **2**, the above results suggest that $\log k_{\mathrm{o}}$ for the reaction of **2** with carboxylate ions should be around 4.5−5.0, which is close to $\log(k_1^{\mathrm{C}})_{\mathrm{o}} = 5.11$ for the reaction of $\mathbf{2}^-$ with *aci*-phenylnitromethane. We conclude that our result for $\log(k_1^{\mathrm{C}})_{\mathrm{o}}$ is reasonable.

For the reaction of *aci*-phenylnitromethane with the 1,3-indandionyl anion, $\log(k_1^{\mathrm{C}})_{\mathrm{o}} = 4.97$ is obtained if one assumes $k_1^{\mathrm{C}} \gg k_1^{\mathrm{C}*}$ and $k_{-1}^{\mathrm{CH}} \gg k_{-1}^{\mathrm{HC}} K_{\mathrm{T}}$, and a $\log(k_1^{\mathrm{C}*})_{\mathrm{o}} = 7.20$ if the opposite assumption ($k_1^{\mathrm{C}*} \gg k_1^{\mathrm{C}}$, $k_{-1}^{\mathrm{HC}} K_{\mathrm{T}} \gg k_{-1}^{\mathrm{CH}}$) is made. The fact that the calculated $\log(k_1^{\mathrm{C}})_{\mathrm{o}} = 4.97$ is higher than $\log k_{\mathrm{o}} = 4.53$ for the protonation of 1,3-indandionyl anion by carboxylic acids[11] may be taken as suggestive evidence that the oxygen to oxygen proton transfer pathway, $(k_1^{\mathrm{C}*})_{\mathrm{o}}$, contributes significantly or may actually be dominant. The $\log(k_1^{\mathrm{C}*})_{\mathrm{o}} = 7.20$ estimate based on this assumption is about 1.3 log units below what one would expect in aqueous solution[13,14] but is consistent with recent results on oxygen to oxygen proton transfers in pure $\mathrm{Me_2SO}$.[15]

B. $\log(k_2^{\mathrm{C}})_{\mathrm{o}}$ for 9-Cyanofluorene and 4-Nitrophenylacetonitrile. The intrinsic rate constants or intrinsic barriers estimated for the carbon to carbon proton transfer between phenylnitromethane and 9-cyanofluorenyl anion ($\mathbf{2}^-$) ($\log(k_2^{\mathrm{C}})_{\mathrm{o}} = 0.01$, $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/C^-}) = 17.05$ kcal/mol) or between phenylnitromethane and 4-nitrophenylacetonitrile anion ($\mathbf{4}^-$) ($\log(k_2^{\mathrm{C}})_{\mathrm{o}} = -0.33$, $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/C^-}) = 17.50$ kcal/mol) allow us to test the relative merits of the "amine method" and the "9-cyanofluorene method" used to estimate intrinsic barriers of identity reactions (see Introduction). $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/C^-})$ can be calculated by the Marcus relationship

$$\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/C^-}) = \frac{1}{2}\{\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/S^-}) + \Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{CH/C^-})\} \quad (25)$$

using the $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/S^-})$ and $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{CH/C^-})$ values from Table 1. The intrinsic barriers and intrinsic rate constants calculated via eq 25 based both on the "amine method" and the "9-cyanofluorene method" are summarized in Table 6, along with the experimental values. The $\log(k_2^{\mathrm{C}})_{\mathrm{o}}$ values calculated on the basis of the "amine method" are much lower and the $\Delta G_{\mathrm{o}}^{\ddagger}$ values much higher than the experimental ones. On the other hand, there is good agreement between the experimental parameters and those calculated on the basis of the "9-cyanofluorene method." Hence our results support this latter method for the calculation of the identity barriers in Table 1, and by implication, they show the validity of the Marcus equation 25 for these two examples.[16]

Table 6. Comparison of Experimental Intrinsic Rate Constants and Intrinsic Barriers with Those Calculated via Equation 25

	experimental		"amine method"		"9-cyano-fluorene method"	
	$\log(k_2^{\mathrm{C}})_{\mathrm{o}}$[a]	$\Delta G_{\mathrm{o}}^{\ddagger}$	$\log(k_2^{\mathrm{C}})_{\mathrm{o}}$[a]	$\Delta G_{\mathrm{o}}^{\ddagger}$	$\log(k_2^{\mathrm{C}})_{\mathrm{o}}$[a]	$\Delta G_{\mathrm{o}}^{\ddagger}$
$\mathrm{PhCH_2NO_2} + \mathbf{2}^-$	0.0	17.0	−1.5	19.0	0.3	18.1
$\mathrm{PhCH_2NO_2} + \mathbf{4}^-$	−0.3	17.5	−2.3	20.1	−0.4	17.7

[a] From Table 5.

C. $\mathrm{Log}(k_2^{\mathrm{C}})_{\mathrm{o}}$ and $\log(k_2^{\mathrm{C}*})_{\mathrm{o}}$ for 1,3-Indandione and Meldrum's Acid. In the reactions of phenylnitromethane with the anions of 1,3-indandione and Meldrum's acid, the distinction between carbon to oxygen ($k_2^{\mathrm{C}*}$) or carbon to carbon (k_2^{C}) proton transfer can be made as follows. The $\log(k_2^{\mathrm{C}*})_{\mathrm{o}}$ values, estimated on the basis of the assumption that carbon to oxygen proton transfer is dominant, are 2.70 ($\mathbf{3}^-$) and >2.87 ($\mathbf{8}^-$), respectively. These estimates may be compared to $\log k_{\mathrm{o}} = 1.88$ for the deprotonation of phenylnitromethane by carboxylate ions.[8] The much larger $\log(k_2^{\mathrm{C}*})_{\mathrm{o}}$ values strongly suggest that the carbon to carbon proton transfer contributes significantly to the reaction and is actually the dominant pathway, with $\log(k_2^{\mathrm{C}})_{\mathrm{o}} \approx 0.28$ for $\mathbf{3}^-$, $\log(k_2^{\mathrm{C}})_{\mathrm{o}} \approx -0.24$ for $\mathbf{8}^-$.

For the 1,3-indandione reaction, this conclusion may be tested with the Marcus equation (eq 25). Using $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/S^-}) = 20.17$ kcal/mol and $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{CH/C^-}) = 14.37$ kcal/mol for CH = **3** ("9-cyanofluorene method," Table 1) yields $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{SH/C^-}) = 17.27$ kcal/mol or $\log(k_2^{\mathrm{C}})_{\mathrm{o}} = -0.15$. This value is well within the uncertainty limits of the experimental $\log(k_2^{\mathrm{C}})_{\mathrm{o}} = 0.28 \pm 0.57$. For the Meldrum's acid reaction, $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{CH/C^-})$ is not known, which precludes the use of eq 25.

D. $\mathrm{Log}(k_2^{\mathrm{C}})_{\mathrm{o}}$ and $\log(k_2^{\mathrm{C}*})_{\mathrm{o}}$ for Nitromethane. As was found for the reaction of phenylnitromethane with 1,3-indandionyl anion, $\log(k_2^{\mathrm{C}*})_{\mathrm{o}} = 2.54$ for the reaction with the nitromethane anion is too high to be accounted for by carbon (of SH) to oxygen (of $\mathrm{CH_2{=}NO_2^-}$) transfer if the deprotonation of phenylnitromethane by carboxylate ions is used as a guide ($\log k_{\mathrm{o}} = 1.88$).[8] We conclude that the carbon to carbon proton transfer pathway is dominant, with $\log(k_2^{\mathrm{C}})_{\mathrm{o}} = -1.04$. Here an independent test via eq 25 is not feasible because $\Delta G_{\mathrm{o}}^{\ddagger}(\mathrm{CH/C^-})$ is not known.

E. $\log(k_2^{\mathrm{C}})_{\mathrm{o}}$ and $\log(k_2^{\mathrm{C}*})_{\mathrm{o}}$ for Acetylacetone. In contrast to the reactions with 1,3-indandionyl, Meldrum's acid, and nitromethide anions, the reaction with the acetylacetonate ion occurs mainly through an enolate oxygen. There are two points that support this conclusion. (1) $\log(k_2^{\mathrm{C}})_{\mathrm{o}} = 1.61$, calculated assuming carbon to carbon proton transfer, is much higher than $\log(k_2^{\mathrm{C}})_{\mathrm{o}} = 0.28$ for 1,3-indandione, a result that is difficult to explain in view of the close similarity between $\log k_{\mathrm{o}}$ for the reaction of acetylacetone and 1,3-indandione with primary amines, the piperidine/morpholine pair, and car-

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(16) A reviewer has suggested that since eq 25 only works when the identity barriers obtained by the "9-cyanofluorene method" are used but not with those from the "amine method," the "...logical conclusion is that the Marcus treatment works in some instances but not in others. So a conclusion that only mentions the validity of the Marcus treatment appears to me unjustified." Our response is that the fact that eq 25 breaks down for the "amine method" only uncovers the deficiencies in using the "amine method" to calculate identity barriers, it does not invalidate the Marcus treatment.

boxylate ions.[11,13] (2) The $\log(k_2^{C*})_o$ value (1.53) calculated by assuming the carbon to oxygen proton transfer is dominant is close to that for the deprotonation of phenylnitromethane by carboxylate ions (1.88).[8]

The fact that the reaction with the acetylacetonate ion is dominated by the carbon to oxygen proton transfer, while the reactions with the anions of 1,3-indandione, Meldrum's acid, and nitromethane are dominated by the carbon to carbon proton transfer can be understood as follows. In the case of acetylacetone, the enol form has a similar pK_a as the keto form (Table 5). Since deprotonation of carbon acids by an oxyanion is typically faster than deprotonation by a carbanion of similar basicity,[12,17] it is not surprising that the carbon to oxygen proton transfer pathway dominates. In the other three cases, the pK_a of the enol (or nitronic acid) is substantially lower than that of the keto (or nitro) form (Table 5). Hence the intrinsically higher kinetic reactivity of the oxygen compared to carbon is offset by its lower basicity in the anions of 1,3-indandione, Meldrum's acid, and nitromethane (Table 5), and the carbon to carbon proton transfer pathway becomes dominant.

Conclusions

(1) In the reaction of phenylnitromethane with the anions of 9-cyanofluorene and 4-nitrophenylacetonitrile, no ambiguity exists with respect to the type of proton transfer observed, i.e., τ_1^{-1} represents oxygen (of the *aci*-form of phenylnitromethane) to carbon proton transfer, and τ_2^{-1} refers to carbon to carbon proton transfer.

(2) The estimated $\log(k_1^{C})_o$ for the reaction of *aci*-phenylnitromethane with 9-cyanofluorenyl anion is "reasonable", since it is similar to that estimated for the reaction of a carboxylic acid with 9-cyanofluorenyl anion. The estimated $\log(k_2^{C})_o$ values for the carbon to carbon proton transfer between phenylnitromethane and 9-cyanofluorenyl or 4-nitrophenylacetonitrile anion are, within their experimental uncertainties, equal to their values calculated by the Marcus equation (eq 25) on the basis of identity reaction barriers derived by the "9-cyanofluorene method." This agreement not only shows that the "9-cyanofluorene method" is better than the "amine method" but *it also strongly supports the validity of the Marcus equation that relates intrinsic barriers of carbon to carbon proton transfer cross reactions to the intrinsic barriers of the corresponding identity reactions.*

(3) The fast reactions (τ_1^{-1}) of phenylnitromethane with the anions of 1,3-indandione, Meldrum's acid, acetylacetone, and nitromethane may, in principle, proceed either by an oxygen (of HS) to carbon or oxygen (of HS) to oxygen proton transfer. For the only case where this process was measurable (1,3-indandione), the evidence points to oxygen to oxygen proton transfer.

(4) For the slow reactions (τ_2^{-1}) of phenylnitromethane with the anions of 1,3-indandione, Meldrum's acid, acetylacetone, and nitromethane, the two possible pathways are carbon to oxygen and carbon to carbon proton transfer. With 1,3-indandione, Meldrum's acid and nitromethane the results are consistent with carbon to carbon proton transfer. In contrast, with acetylacetone, carbon to oxygen proton transfer appears to be dominant, because the pK_a value of the enol form is comparable to that of the keto form.

Experimental Section

Methods. Most carbon acids were available from previous studies (phenylnitromethane,[8] 9-cyanofluorene,[5] 1,3-indandione,[11] 4-nitrophenylacetonitrile,[18] acetylacetone,[13] and nitromethane[8]). Meldrum's acid was synthesized by the method of Davison and Bernhard,[19] mp 94.5–95.5 °C (lit.[19] 94–95 °C).

Reaction Solutions and pH and pK_a Measurements. 90% Me_2SO–10% water (v/v) was prepared by adding, e.g., 10 mL of water to a 100-mL volumetric flask and filling to volume with Me_2SO. pH measurements were made in mock solutions with a Corning No. 476022 glass electrode and a Beckman No. 39400 calomel reference electrode on an Orion 611 pH meter. The meter was calibrated with buffers according to the method of Hallé et al.[20] All reaction solutions were adjusted to have an ionic strength of 0.06 M by addition of KCl.

The pK_a of *p*-nitrophenylacetonitrile was determined by classical spectrophotometric procedures, exploiting the large difference in the extinction coefficients of the acid and base form. $pK_a = 12.03 \pm 0.03$ was obtained as the average of six measurements in piperidine buffers of pH 11.66–12.28. The pK_a values of the other carbon acids were known.

Rate Measurements. Rates were determined spectrophotometrically either in a Durrum-Gibson stopped-flow or conventional Perkin-Elmer Model 559A spectrophotometer. With the 4-nitrophenylacetonitrile, nitromethane, and acetylacetone buffers, the reactions were initiated by mixing a slightly acidic solution of phenylnitromethane with the buffer solution. In order to minimize decomposition of the buffer anion in the buffer stock solution, it was found advantageous to generate the buffer anion just prior to reaction as follows. The buffer was placed into the same stopped-flow syringe as the slightly acidic phenylnitromethane solution. This assured that all the buffer was present in the CH form. Reaction was then initiated by adding an appropriate amount of KOH which would be sufficient to neutralize the excess acid in the phenylnitromethane solution and to produce the desired [CH]:[C^-] ratio.

With the 9-cyanofluorene, 1,3-indandione, and Meldrum's acid buffers, the reactions were conducted in the reverse direction, i.e., by mixing the acidic buffer with a basic solution of the phenylnitromethide anion (pH jump). The phenylnitromethide anion was generated immediately before the pH jump.

The wavelength for monitoring the reactions was chosen so as to minimize interference between the spectrum of the phenylnitromethide (or *aci*-form of phenylnitromethane) and that of the buffer anion. The following wavelengths were used. 9-Cyanofluorene, 348 nm (τ_1^{-1} and τ_2^{-1}); 1,3-indandione, 334 nm (τ_1^{-1}), 282 nm (τ_2^{-1}); 4-nitrophenylacetonitrile, 338 and 356 nm (τ_2^{-1}); Meldrum's acid, 292 nm (τ_2^{-1}); acetylacetone, 328 nm (τ_2^{-1}); nitromethane, 326 nm (τ_2^{-1}).

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Supplementary Material Available: Figures S1–S2, representative plots of the reaction of phenylnitromethane (2 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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