Rates of Proton Abstraction from 4-Nitrobenzyl Halides

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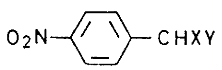
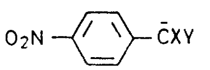
The rates of proton abstraction and carbanion protonation for 4-nitrobenzyl halides in aqueous and methanolic dimethyl sulphoxide have been determined. In addition, measurements have been made on some benzylidene and bis-(4-nitrophenyl)methyl halides in aqueous dimethyl sulphoxide. The effects of introducing a second halogen atom or a 4-nitrophenyl group upon both kinetic and thermodynamic acidities are discussed in terms of carbanion structure and solvent effects.

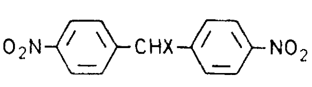


(1)

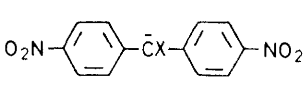


(2)

a; X = H, Y = F
b; X = H, Y = Cl
c; X = H, Y = Br
d; X = H, Y = I
e; X = Y = H
f; X = Y = Cl
g; X = Y = Br



(3)



(4)

a; X = Cl
b; X = Br
c; X = H

THE reactions of hydroxide and alkoxide ions with 4-nitrobenzyl halides of general structures (1) and (3) under various experimental conditions (*e.g.*, different solvent mixtures, absence or presence of oxygen) have received considerable attention in recent years.[1-6] Although some controversy still exists regarding the mechanistic schemes proposed to account for the various final products of these reactions, it is generally believed that they all proceed *via* a base-initiated deprotonation of the halides, to give the carbanions (2) and (4), as an initial, rapid step [equation (1)]. As part of a general

$$(1)[\text{or }(3)] + \left\{\begin{matrix}OH^-\\ CH_3O^-\end{matrix}\right. \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (2)[\text{or }(4)] + \left\{\begin{matrix}H_2O\\ CH_3OH\end{matrix}\right. \qquad (1)$$

study of the behaviour of 4-nitrobenzyl halides in basic media we have compared the rates of proton abstraction from these compounds. Combination of these data with those for the parent compounds (1e) and (3c) should provide valuable information on the extent to which the stabilities of the carbanions (2) and (4) are affected by changes in the nature of the halogen atom, or by the introduction of a second halogen atom or 4-nitrophenyl group.

Carbon acids, in general, react with bases at markedly lower rates than do nitrogen or oxygen acids of the same, or comparable, acid strength.[7-10] The weak acidity of most compounds (1) and (3) necessitates proton abstraction measurements in media quite different from those used for analogous compounds studied previously, *i.e.*, 2,4,6-trinitrotoluene,[11,12] 4-nitrobenzyl cyanide,[13] 1-aryl-1-nitroethanes.[10b] To obtain comparable data for the compounds studied we have therefore had to resort to hydroxide ion in aqueous dimethyl sulphoxide, or methoxide ion in methanolic dimethyl sulphoxide, as bases, and we report here the results of these investigations.

EXPERIMENTAL

Materials.—The compounds studied were either commercial products, or were synthesized according to standard procedures. They were all recrystallized at least twice and carefully dried immediately prior to use, and in all cases m.p.s agreed with the reported values. Solutions of aqueous potassium hydroxide and methanolic potassium methoxide in dimethyl sulphoxide (DMSO) were prepared as previously described.[14,15]

Rate Measurements.—Kinetic studies were performed by using a Durrum stopped-flow spectrophotometer in which the cell compartment was thermostatted to ±0.5 K. All runs were carried out under first-order conditions, with a substrate concentration in the range 2—10 × 10^{-5}M and base concentrations in the range 5 × 10^{-4}—1 × 10^{-1}M. Rate constants are considered accurate to ±5%.

RESULTS AND DISCUSSION

In Figure 1 are shown two representative oscilloscope traces obtained from reactions of hydroxide and methoxide ions with compounds of general structures (1) and (3), respectively, in DMSO solutions. Mixing the substrate and base resulted in the rapid appearance of yellow or purple transient species whose visible spectra were recorded. The spectra obtained show broad absorption bands typical of carbanions, as illustrated in Figure 2 for (2b) and (4a). The long-wavelength band maxima range from 385 for (2a) to 450 nm for (2f), *cf.* 490 nm for the anion formed from 4-nitrophenylnitromethane in acetonitrile [16] and *ca.* 530 nm for the anion

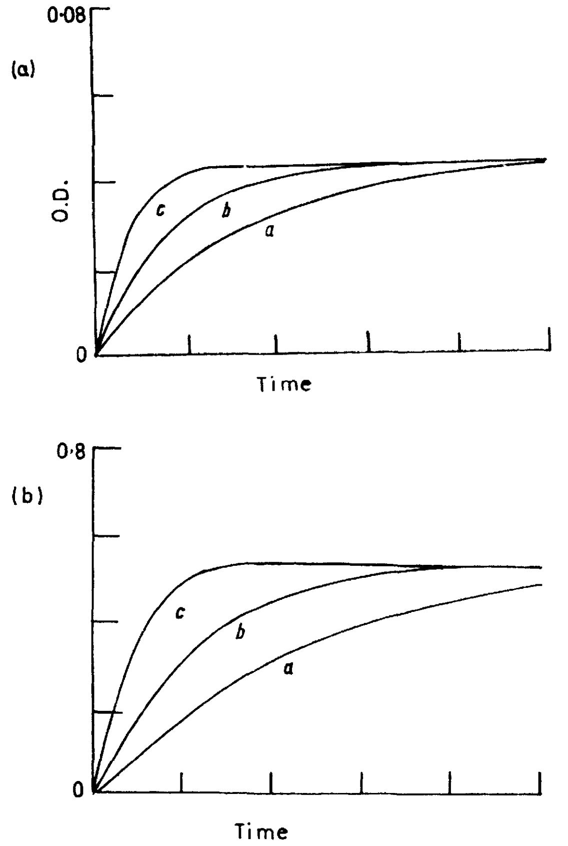


FIGURE 1 Representative oscilloscope traces illustrating carbanion formation at 293 K; curves *a*—*c* corresponding to 0.2, 0.4, and 1 s per time-scale division respectively: (a) [(3a)] 2.6 × 10^{-5}M; [OH^-] 1.5 × 10^{-2}M in 70% DMSO–30% H_2O, measured at 760 nm; (b) [(1b)] = 3.0 × 10^{-5}M; [OH^-] = 7.0 × 10^{-3}M in 90% DMSO–10% H_2O, measured at 450 nm

formed from 4-nitrobenzyl cyanide in methanol-DMSO mixtures.[17] For the diaryl carbanions, values lie in the range 710 for (4c) to 770 nm for (4b). The result for (4c) compares well with the value of 704 nm for ethanolic DMSO, obtained by Bowden and Stewart,[18] and with the value (770 nm) for 80% acetonitrile–20% ethanol obtained by Leffek.[19]

As can be seen by reference to Figure 1a, the purple intermediate obtained from reaction of the derivative (3a) with hydroxide ion in water–DMSO does not decompose appreciably during the time of measurement, and indeed the intermediates derived from all compounds (3) were stable for considerable periods. Similarly, the yellow species obtained under equivalent experimental conditions from (1f and g) were relatively stable. This allows a check of the reversibility of the systems, and this was carried out by using solutions in 90% DMSO–10% H_2O. The initially formed coloured species were rapidly destroyed by the addition of hydrochloric acid, but were regenerated by the addition of an excess of potassium hydroxide solution (in the same solvent mixture). The optical densities of the final solutions agreed to within ±5% with those calculated from the known extinction coefficients, indicating that the observed reactions are reversible. Regeneration of the starting materials on addition of hydrochloric acid confirms that these are reversible proton-transfer reactions and that the coloured species are the carbanions. Similar reversibility experiments were successfully performed on (1b and c) in 95% DMSO–5% H_2O, where the carbanions are much more stable than in the 90% DMSO–10% H_2O mixture used for kinetic studies, identical spectra being obtained for both solutions. In contrast, solutions of the intermediates formed from (1a, d, and e) were not sufficiently stable to permit reversibility tests as described above but, by analogy, we have assumed the coloured species present in these solutions to be the carbanions.

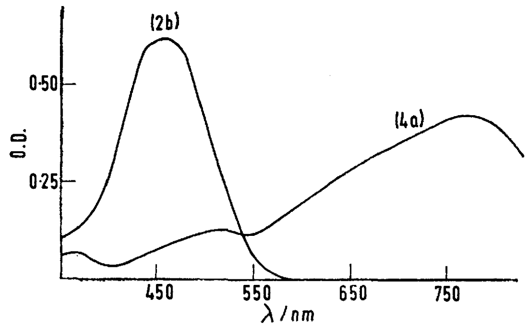


FIGURE 2 Typical absorption spectra of carbanions: (2b) in 90% DMSO–10% CH_3OH and (4a) in 80% DMSO–20% H_2O

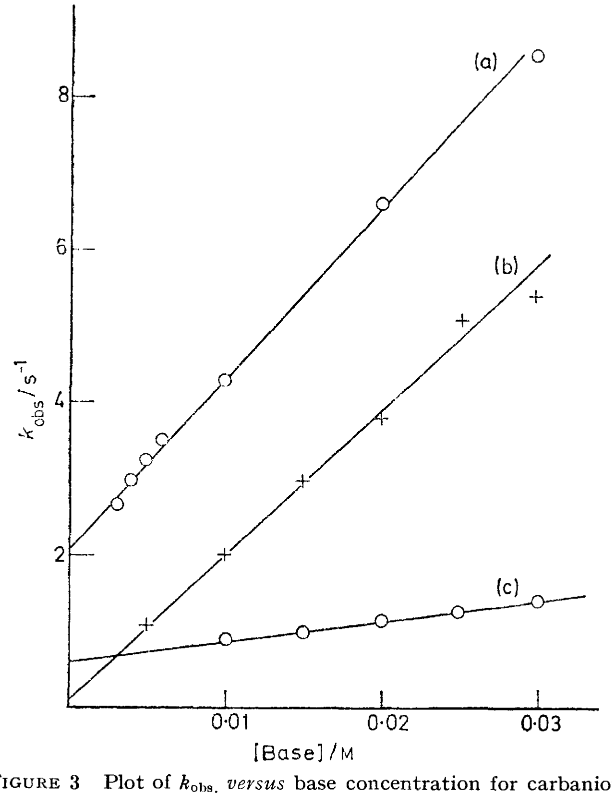


FIGURE 3 Plot of $k_{obs.}$ *versus* base concentration for carbanion formation: (a) (2b) in 90% DMSO–10% CH_3OH at 283 K; (b) (4a) in 70% DMSO–30% H_2O at 293 K; (c) (4b) in 60% DMSO–40% H_2O at 293 K

TABLE 1

Rate coefficients of proton abstraction by methoxide ion, k_1, and carbanion reprotonation, k_{-1}, for 4-nitrobenzyl halides in 90% DMSO–10% CH_3OH at various temperatures and their derived thermodynamic parameters at 298 K [a]

Compound		283 K	293 K	303 K	$\Delta H^{\ddagger}_1$	$\Delta H^{\ddagger}_{-1}$	$\Delta S^{\ddagger}_1$	$\Delta S^{\ddagger}_{-1}$	ΔH^0	ΔS^0
(1a)	k_1	2.72	5.1	10.8	46.44		−72.0			
	k_{-1}	0.74	1.34	2.1		33.05		−129.7		
	K	3.67	3.80	5.14					13.4	57.7
(1b)	k_1	220	450	980	50.21		−21.8			
	k_{-1}	2.2	4.5	9.5		50.42		−60.2		
	K	100	100	103					~0	38.4
(1c)	k_1	224	470	940	46.23		−29.7			
	k_{-1}	16	33.4	57		44.14		−64.8		
	K	14	14.1	16.5					2.09	35.1
(1d)	k_1	250 [b]	660	1 400 [c]	71.55		54.4			
	k_{-1}	45 [b]	66	112 [c]		34.31		−92.0		
	K	5.55 [b]	10	12.5 [c]					37.24	146.4

[a] Units: k_1/l mol^{-1} s^{-1}; k_{-1}/s^{-1}; K/l mol^{-1}; ΔH/kJ mol^{-1}; ΔS/J mol^{-1} K^{-1}. Errors: activation enthalpies, ±1.67 kJ mol^{-1}; activation entropies, ±5.8 J mol^{-1} K^{-1}. [b] Measured at 284 K. [c] Measured at 301 K.

The kinetic results obtained under conditions of varying base concentration further support the assumption that the coloured solutions are due to carbanion formation. From equation (1), the observed first-order rate constant, $k_{obs.}$, must obey equation (2) where k_1 is the

$$k_{obs.} = k_1[\text{Base}] + k_{-1} \qquad (2)$$

second-order rate constant for proton abstraction and k_{-1} is the first-order rate constant for reprotonation of the carbanion. Plots of $k_{obs.}$ *versus* base concentration are linear, as can be seen from Figure 3, and from these values of k_1 and k_{-1} may be determined, and hence the equilibrium constant K ($= k_1/k_{-1}$) calculated.

The measured rates and calculated equilibrium constants for proton abstraction at various temperatures for the four 4-nitrobenzyl halides (1a—d) in 90% DMSO–10% CH_3OH (v/v) are summarized in Table 1, together with the corresponding activation and thermodynamic parameters for both forward and reverse steps. Analogous results at 293 K for the monoaryl derivatives (1a—g) and the diaryl derivatives (3a—c), in DMSO–H_2O mixtures, are shown in Tables 2 and 3, respectively. Values of k_{-1} for compounds (4a—c) were too small to allow reliable determinations of their values in mixtures containing more than 70% DMSO (v/v). Similarly, because of the unreliability of the data obtained, it was not possible to measure k_1 and k_{-1} values for (1a—g) in the same solvent mixtures for all compounds.

Monoaryl Derivatives.—Inspection of Table 1 shows that k_1 for proton abstraction by methoxide ion in 90% DMSO–10% CH_3OH is *ca.* 100-fold lower for the fluorine-containing compound than for the chlorine, bromine, and iodine analogues, the ratios $k_1^{(1b)}/k_1^{(1a)}$, $k_1^{(1c)}/k_1^{(1a)}$, and $k_1^{(1d)}/k_1^{(1a)}$ being 88, 92, and 129, respectively, at 293 K. Combining the experimental results of Table 2 for 90% DMSO–10% H_2O and 95% DMSO–5% H_2O leads to ratios of the same order of magnitude for proton abstraction by hydroxide ion in these media: $k_1^{(1b)}/k_1^{(1a)} = 120$, $k_1^{(1c)}/k_1{}^{1a)} = 121$, $k_1^{(1d)}/k_1^{(1a)} = 142$ at 293 K.

TABLE 2

Rate and equilibrium data for proton abstraction and carbanion protonation for 4-nitrophenyl derivatives (1) in DMSO–H_2O mixtures at 293 K

Compound	% DMSO (v/v)	k_1/ l mol^{-1} s^{-1}	k_{-1}/ s^{-1}	K/ l mol^{-1}
(1e)	95	17.4	0.22	79
	90	1.51 [a]	0.70 [a]	2.16 [a,b]
	80	≃0.09 [a]	0.80 [a]	0.11 [a]
(1a)	95	32	0.88	36.4
	90	2.75 [a]	2.8 [a]	≃1 [a]
(1b)	90	331	0.24	1 380
	80	19.2	0.27	71
(1c)	90	334	0.42	795
(1d)	95	4 540	0.5	9 100
	90	392	1.6	245
(1f)	80	16 400	15	1 090
	70	1 190	40	29.75
	60	190	35	5.43
(1g)	80	$\simeq 2 \times 10^4$	>100	$\simeq 2 \times 10^2$

[a] Values estimated from the DMSO influence on the rate constants of the chloro and iodo derivatives. [b] Attempts to determine this value indicated that it is very low, in accordance with a higher k_{-1} value, *cf.*, ref. 20.

TABLE 3

Rate and equilibrium data for proton abstraction and carbanion protonation for bis-(4-nitrophenyl) derivatives (3) in DMSO–H_2O mixtures at 293 K

		% DMSO (v/v)				
Compound		50	60	70	80	90
(3a)	k_1/l mol^{-1} s^{-1}	4.05	27.2	188	2 500	6×10^4
	k_{-1}/s^{-1}	0.10	0.18	0.17	≃0.1	*a*
	K/l mol^{-1}	40.5	151.1	1 106	$\simeq 2.5 \times 10^4$	
(3b)	k_1/l mol^{-1} s^{-1}	6	35.8	220	2 280	5.25×10^4
	k_{-1}/s^{-1}	0.52	0.45	0.30	≃0.1	*a*
	K/l mol^{-1}	11.5	80	733	$\simeq 2.3 \times 10^4$	
(3c)	k_1/l mol^{-1} s^{-1}			250	9 500	
	k_{-1}/s^{-1}			0.01	<0.01	
	K/l mol^{-1}			2.5×10^4	$\simeq 1 \times 10^6$	

[a] Values very low, measurements unreliable.

In addition, Table 2 shows that the rate of carbanion formation from 4-nitrotoluene is *ca.* 2-fold less than that for 4-nitrobenzyl fluoride in 95% DMSO–5% H_2O, thus giving an order of kinetic acidities for compounds (1) of (1d) > (1c, b) > (1a) > (1e).

The rates of reprotonation of (2a—d) in 90% DMSO–10% CH_3OH increase in the sequence (2a) < (2b) < (2c) < (2d), giving rise to ratios of $k_{-1}^{(2b)}/k_{-1}^{(2a)}$, $k_{-1}^{(2c)}/k_{-1}^{(2b)}$, and $k_{-1}^{(2d)}/k_{-1}^{(2c)}$ of 3.36, 7.42, and 1.98 respectively at 293 K. However, the same trend is not evident in H_2O–DMSO mixtures where protonation of the fluoro-carbanion occurs at a rate greater than that for either the chloro- or bromo-analogue, *i.e.* in 90% DMSO–10% H_2O $k_{-1}^{(2a)}/k_{-1}^{(2b)} = 11.65$ and $k_{-1}^{(2a)}/k_{-1}^{(2c)} = 6.67$. Similarly, in 95% DMSO–5% H_2O the fluoro-carbanion is protonated more rapidly than the iodo- or protio-derivative; $k_{-1}^{(2a)}/k_{-1}^{(2d)} = 1.76$ and $k_{-1}^{(2a)}/k_{-1}^{(2e)} = 4$.

Combination of the k_1 and k_{-1} results for both aqueous and methanolic DMSO mixtures results in the same order of stabilities of the halogenated carbanions, *i.e.*, Cl > Br > I > F. At 293 K the ratios $K^{(2b)}/K^{(2c)}$, $K^{(2b)}/K^{(2d)}$, and $K^{(2b)}/K^{(2a)}$ are *ca.* 7, 10, and 26 respectively in 90% DMSO–10% CH_3OH, whereas they are 1.7, 5.6, and *ca.* 500 in 90% DMSO–10% H_2O. It is also noteworthy that the fluoro-carbanion is *ca.* 2-fold less stable than the parent hydrogen-containing carbanion in 95% DMSO–5% H_2O ($K^{(2a)}/K^{(2e)}$ 0.46).

Whenever measurements have been carried out in solutions of varying solvent composition, there is an increase in k_1 and a decrease in k_{-1} as the DMSO concentration is increased (Table 2). This is in contrast to the behaviour of 4-nitrobenzyl cyanide in H_2O–DMSO mixtures, where there appears to be a sharp increase in both k_1 and k_{-1} at a mole fraction of DMSO of 0.35.[20] However, these latter results are derived from relaxation measurements made at the limit of the technique used, in the region where anomalous behaviour has often been observed, *i.e.*, $2H_2O$–1DMSO, and may thus reflect unusual solvent effects, *etc.* in this system.

From the results presented, it can be seen that the replacement of a benzylic hydrogen atom of 4-nitrotoluene by fluorine results in a slight increase in kinetic acidity and a slight decrease in the thermodynamic acidity. This is in contrast to the behaviour of the other halogenated analogues, which show appreciable increases in both kinetic and thermodynamic acidities, relative to 4-nitrotoluene, but is not totally unexpected in the light of earlier work. Thus, Hine [21,22] and Streitwieser [23] have both noted that the effect of α-fluorine substituents is generally to decrease the rate of formation of sp^2-hybridized carbanions, but to increase that of sp^3-hybridized carbanions. Also, Adolph and Kamlet reported that the pK_a values for ionization of ethyl nitroacetate, α-nitroacetamide, chloronitromethane, and dinitromethane in water to give sp^2-hybridized carbanions are increased by the introduction of an α-fluoro-substituent, whereas they are all decreased by the introduction of an α-chloro-substituent.[24]

The acid-weakening effect of an α-fluorine atom has been attributed to the destabilization of the sp^2-hybridized carbanion by repulsive electronic interaction with the non-bonding electrons of the fluorine, and/or to the lower stability of the C_{sp^2}–F bond in comparison with the other C_{sp^2}–X bonds (X = halogen).[7,8,22a,25,26] Our results are in accord with these interpretations if the carbanions formed from (1a—e) are sp^2-hybridized, or almost so. Although the planarity of some benzylic anions has been questioned (*e.g.*, that derived from benzal fluoride [23,25]), the presence of the 4-nitro group in the compounds studied here should ensure that the corresponding anions are planar, or almost so. This will maximize the overlap between the π-orbitals of the ring and the exocyclic lone-pair orbital and permit charge delocalization onto the nitro group. The fact that the acidity differences found in the present work between (1a and b) in 90% DMSO–10% CH_3OH (ΔpK 1.42) and in 90% DMSO–10% H_2O (ΔpK 2.7) are of the same order of magnitude as those between α-fluoro-α-nitro- and α-chloro-α-nitro-acetamide (ΔpK 2.39), and between ethyl α-fluoro-α-nitro-acetate and ethyl α-chloro-α-nitro-acetate (ΔpK 2.12) lends some support to this conclusion.

Comparison of the results for the ionization of (1b) with that for (1f) shows that the introduction of the second chlorine atom increases both the kinetic and the equilibrium acidity, as expected. However, the increase in K is very much less than that in k_1 ($K^{(2f)}/K^{(2b)}$ *ca.* 15; $k_1^{(1f)}/k_1^{(1b)}$ *ca.* 850) because of the marked increase in the rate of carbanion protonation, $k_{-1}^{(2f)}/k_{-1}^{(2b)}$ *ca.* 55. Although precise data could not be obtained for (1g), the introduction of a second bromine atom into (1c) clearly results in increases in both k_1 and k_{-1}. The smaller sensitivity of K to the introduction of the second halogen atom, in comparison to the effect upon k_1, is interesting (*i.e.*, a Brönsted coefficient >1) but not totally unexpected. Thus, Bordwell found that structural changes in aryl-nitroethanes and -nitromethanes resulted in greater effects upon their kinetic acidities than upon the corresponding equilibrium acidities.[10] This behaviour has so far been noted only for carbon acids and is attributed to the extensive structural reorganization which accompanies carbanion formation.[10]

Diaryl Derivatives.—A comparison of the results in Tables 2 and 3 shows clearly that the bis-(4-nitrophenyl) carbanions (4) are much more stable than their monoaryl analogues (2), the introduction of a second 4-nitrophenyl group causing both a large increase in k_1 and an appreciable decrease in k_{-1}. Increased stabilization of the diaryl carbanions would be expected from the possibility of delocalization of the negative charge into the extra phenyl ring, but it is of interest to note that the effect upon both rate and equilibrium constants is much greater for the hydrogen-containing derivative (3c) than upon the halogen-containing derivatives (3a and b). Thus between 4-nitrotoluene and bis-(4-nitrophenyl)-methane there is a 10^5-fold increase in k_1 and a 10^2-fold decrease in k_{-1}, leading to a 10^7-fold increase in K for the diaryl compound. In contrast, similar considerations for the corresponding α-halogenated compounds reveal 10^2-fold increases in k_1, *ca.* 3-fold differences in k_{-1}, and thus *ca.* 300-fold increases in K. As a result, the thermodynamic acidity of (3c) is *ca.* 25-fold greater than that of (3a or b), whereas the thermodynamic acidity of (1e) is more than two orders of magnitude lower than that of (1b or c).

A tentative explanation of this observation, based upon the recent proposals of Slater and Chan to account for the rate of deprotonation of phenylnitromethane in H_2O–DMSO mixtures,[27] is to attribute these differences to differential solvent interaction in the transition states for carbanion protonation. Assuming that the transition state for protonation of (2) or (4) involves a reasonable degree of formation of the C–H bond and a partial transfer of a proton from water to the anion, then the greater the unfavourable solvation energy difference between carbanion and hydroxide ion the more difficult will be the attainment of this transition state in solutions containing high percentages of DMSO. The stabilization energy gain on replacing the hydroxide ion by the delocalized diaryl carbanion should be greater for the hydrogen-containing compound (3c), than for the halogenated derivatives (3a and b), because of the possibility of the energetically unfavourable interaction of the residual charge on the exocyclic carbon atom with the halogen atom lone-pair electrons in the anions derived from these latter compounds. Hence the solvent reorganization may be less for protonation of (4a or b) than of (4c), leading to a lower k_{-1} value for the latter carbanion. Such an effect would not necessarily be evident in the monoaryl series where the residual charge on the exocyclic atom is greater, and the steric constraints upon solvation fewer, than in the diaryl compounds. The smaller differences in k_{-1} values between (2e) and (2a—d) than between (4c) and (4a or b) are in accord with such an explanation.

We are grateful to the Coopération France-Québec for financing the exchanges between our laboratories, and to the National Research Council of Canada for financial support.

[8/1853 *Received*, *23rd October*, 1978]

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