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THE SOLVATION AND NUCLEOPHILICITY OF CARBANIONS

KINETICS AND THE MECHANISM OF CONDENSATION OF NITRO COMPOUNDS WITH ACETALDEHYDE IN DIMETHYLSULFOXIDE

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Abstract—The kinetics and mechanism of the condensation of nitro compounds with a carbonyl group were investigated in DMSO, the addition of 1,1-dinitroethane to acetaldehyde being used as a model reaction. The acid-catalysed addition of the nitro compound anion to the CO group is the rate-limiting stage of the process. Equilibrium and rate constants for this particular stage were determined for 1,1-dinitroethane and methyl-α-nitropropionate anions which characterise the carbon basicities and carbon nucleophilicities of these anions. The correlation between the basicities and nucleophilicities of the two anions in DMSO is "normal". The more basic anion reacts faster than the less basic one.

It is suggested that the unusual correlation between the basicities and nucleophilicities of nitro compound anions previously observed in water is due to the specific solvation of anions by H-bonds.

THE assumption that the relative stabilities of reaction products are reflected in the corresponding transition states, which implies a correlation between the rates of reactions and their equilibria, is the basis for linear free energy relationships. The scope and limitation of this generalization and the reasons for its non-applicability in certain cases are problems of fundamental importance.

The unusual correlations of rates and equilibria are to be found in the field of ambident anion reactivity where anion basicities* and nucleophilicities* towards a given electrophile are often antiparallel.

For example, Pearson[2] noticed that in water the dinitromethane anion abstracts a proton from H_3O^+ faster than the nitromethane anion does, the latter being a 10^6 times stronger base. Bordwell *et al.*[3,4] have recently reported the unusual (less than 0) Brönsted coefficients in some nitroalkane anion protonation reactions. We have shown[5,6] that this anomalous correlation between basicity and nucleophilicity is a general feature of the nitro compound anion reactivity which is displayed towards carbon acids, as well as towards the proton.

We have suggested[7] that anomalous correlations observed in protic media, are due to the specific solvation of ambident anions by H-bonding with the protic solvent. In an attempt to prove this, we examined this correlation for nitro compound anions in a dipolar aprotic medium where solvation of anions by hydrogen bonds is impossible.

The effects of the solvent on the hydrogen basicity of nitro compound anions have been given considerable attention,[8-14] whereas the dependence of the correlation between basicity and nucleophilicity upon the type of solvent has not hitherto been investigated.

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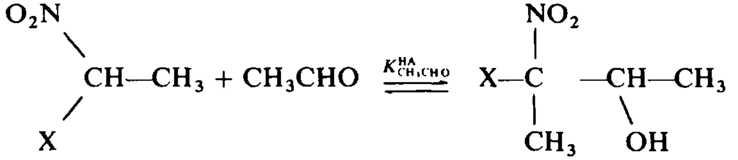
* The terminology suggested by J. Hine[1]

To achieve this we calculated the equilibrium and the rate constants for nucleophilic addition of 1,1-dinitroethane and methyl α-nitropropionate anions to acetaldehyde in dimethylsolphoxide (DMSO) and compared the results with the analogous data for a water solution.

RESULTS

Using the spectrophotometer technique we measured the equilibrium constants ($K^{HA}_{CH_3CHO}$) and the rates of both the forward and reverse reactions 1.



(1)

(HA) (CH$_3$CHAOH)

where X = NO_2; – $COOCH_3$.

The respective $K^{HA}_{CH_3CHO}$ values were found to be 300 ± 70* M^{-1} for 1,1-dinitroethane and 170 ± 20* M^{-1} for methyl α-nitropropionate.

The $K^{HA}_{CH_3CHO}$ for methyl α-nitropropionate in water was previously determined with a large experimental error.[15] In the present paper we measured it again employing the more reliable potentiometer technique, and found it to be 15·4 ± 2M^{-1}. A more detailed description of the $K^{HA}_{CH_3CHO}$ determination is given in the Experimental.

The velocities of the forward and reverse reactions (1) were measured in various buffer solutions in DMSO at 25° and constant ionic strength ($\mu = 0{\cdot}05$). In all runs the concentrations of nitro compounds were negligible, as compared with those of the buffer components or acetaldehyde. Under experimental conditions used both the forward and reverse reactions were essentially irreversible.

The condensation of 1,1-dinitroethane with acetaldehyde was chosen as a model reaction for studying the mechanism of the nitro alcohol formation in a dipolar aprotic medium. We investigated its kinetics in the following buffer solutions in DMSO: salycilic acid-potassium salycilate; dichloroacetic acid-potassium dichloroacetate; monochloroacetic acid- potassium nonochloroacetate and triethylamine-triethylammonium perchlorate. We also measured the rates of 3,3-dinitro-2-butanol formation in solutions containing dichloroacetic acid, potassium dichloroacetate and succinic acid (the concentrations of the former two being constant and that of the latter being variable) and we found that the rates of nitro alcohol formation always exhibited a first order dependence on the nitro compound concentration.

The pseudo first-order rate constant k_{obs} in a buffer of a given composition is directly proportional to the acetaldehyde concentration. A typical plot for k_{obs} *vs* [CH_3CHO] is shown in Fig 1. The slope gives the pseudo second-order rate constant (k''_{obs}) for the reaction in the given buffer solution.

The k''_{obs} value depends on the buffer capacity and the buffer components' ratio for all the buffers studied. The plot of k''_{obs} *vs* analytical concentration of the buffer components (C_{HB}; C_{B^-}) (when their ratio is constant) is a curve. (Fig 2). However, in

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* Standard deviation.

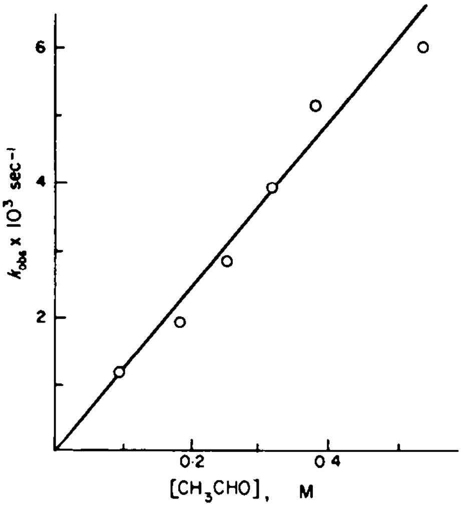


FIG 1. Plot of k_{obs} for the 3,3-dinitrobutan-2-ol formation *vs* [CH$_3$CHO]. Buffer: dichloroacetic acid-potassium dichloroacetate 0·05 M :0·05 M

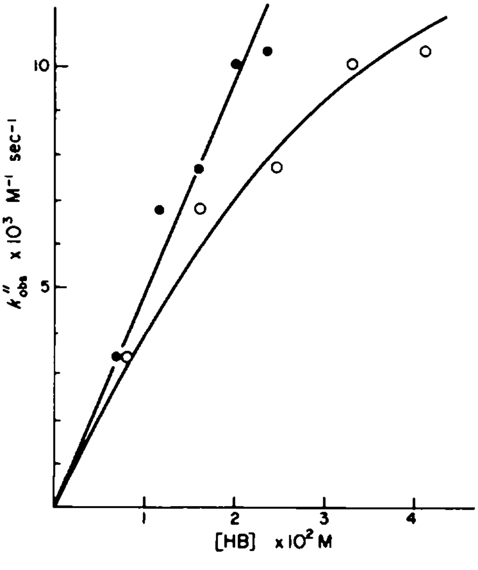


FIG 2. Plot of k''_{obs} for the 3,3-dinitrobutan-2-ol formation *vs* concentrations of buffer components. Buffer: salicilic acid-potassium salycilate 1 :1.
○k''_{obs} *vs* $C_{HB} = C_B$
●k''_{obs} *vs* [HB] = [B$^-$]

dipolar aprotic media the analytical concentrations of the components do not reflect the actual concentration of the active species due to various associative processes (e.g. ion-pairing or homoconjugation).

Kolthoff has determined the equilibrium constants for ion-pairing (Ki.p.) in acetonitrile for a number of sodium and potassium salts of phenols and carboxylic acids[16-18] whose acidities in aprotic media are comparable to those of the buffer acids used in the present paper. We assumed that the Ki.p's for the respective salts we used are comparable to those of the salts studied by Kolthoff. Having taken into account Parker's solvent activity coefficients[19] for the corresponding cations and anions for transition from acetonitrile to DMSO, we came to the conclusion that ion-paring should be negligible for the potassium salts used in DMSO.

The homoconjugation constant ($K_{HB\bar{2}}$) for salycilic acid is equal to $30M^{-1}$.[20] Using this value, we calculated the concentrations of the non-associated ("free") buffer components in the salycilate buffers. Fig 2 shows that k''_{obs} is directly proportional within experimental error to the concentrations of "free" components ([HB]; [B⁻]). For quite a number of carboxylic acids and phenols the $K_{HB\bar{2}}$-values range from $30M^{-1}$ up to $60M^{-1}$.[20] We assumed that the $K_{HB\bar{2}}$-values for di- and monochloroacetic acids also come within this range. This is confirmed by the estimation of the approximate $K_{HB\bar{2}}$-value for dichloroacetic acid, 60 ± $30M^{-1}$ (Experimental). The value 60, giving the best linear relationship between k''_{obs} and the concentration of "free" buffer components, appears to be the most appropriate.

A change in the $K_{HB\bar{2}}$-value for monochloroacetic acid from 30 to 60 brought about only a 10% change in the slope of the corresponding linear plot. The average value of $K_{HB\bar{2}}$ was adopted.

As the homoconjugation of triethylamine with its conjugate acid is negligible in acetonitrile,[21] one may assume it to be even smaller in more basic DMSO.

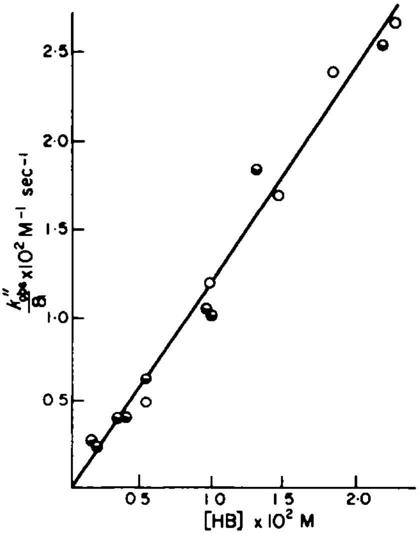


Fig 3. Plot of k''_{obs}/α for the 3,3-dinitrobutan-2-ol formation *vs* [HB]. Buffer: dichloroacetic acid-potassium dichloroacetate.

○ $\frac{C_{HB}}{C_{B^-}} = 1$ ◐ $\frac{C_{HB}}{C_{B^-}} = 2$

Allowances being made for the homoconjugation effect, we found the k''_{obs} value to be directly proportional to the concentrations of the "free" buffer component for all the buffers studied. This implies that one of the two buffer components is kinetically active. The question as to whether HB or B^- is the active species is solved by considering the k''_{obs} values for buffer solutions with different component ratios. Assuming that nitro compounds react only in their anion form, the second-order rate constants observed were divided by α-values (α is the ratio of the concentration of the nitro compound anion to the analytical concentration of the nitro compound in a given buffer) in order to take account of the incomplete dissociation of the 1,1-dinitroethane in the buffers used.

In Fig 3 the k''_{obs}/α values are plotted against the concentration of the "free" buffer acid [HB] and shows that a doubling of the basic component concentration does not affect the k''_{obs}/α value, provided that [HB] remains constant (the points corresponding to $C_{HB}/C_{B^-} = 1$ and $C_{HB}/C_{B^-} = 2$ correspond to the same straight line). It follows that only the buffer acid is a kinetically active species.

The plot of k''_{obs} for the formation of 3,3-dinitro-2-butanol in a given dichloroacetate buffer *vs* concentration of succinic acid added to this buffer is shown in Fig 4. Succinic acid, which is 3·2 powers of ten weaker than dichloroacetic acid (Experimental), is practically undissociated in these solutions. Thus, adding small amounts of succinic acid does not affect the pH values of the dichloroacetic buffers and so the degree of dissociation in 1,1-dinitroethane remains essentially unchanged. The k''_{obs} increases linearly with the succinic acid concentration (Fig 4), the intercept of the plot being equal to the k''_{obs} value in the pure dichloroacetic buffer. In view of these results, it may be concluded that the acidic species participate in the rate limiting

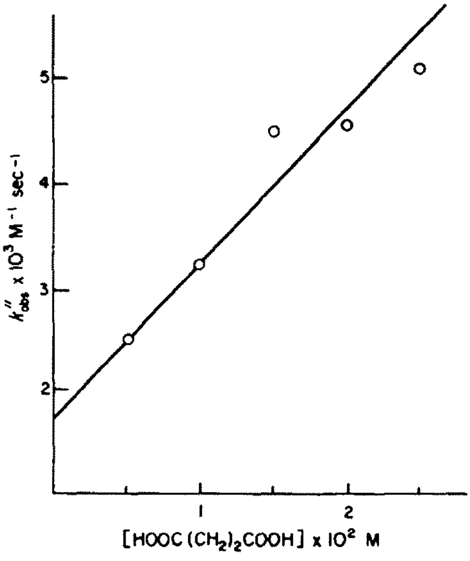


FIG 4. Plot of k''_{obs} for the 3,3-dinitrobutan-2-ol formation in a buffer concentration of succinic acid. Buffer: dichloroacetic-potassium dichloroacetate 0·0078 M : 0·0078 M

stage of nitro alcohol formation. The reaction velocity of the overall process is expressed by the equation:

$$v = \alpha \cdot [\mathrm{HA}] \cdot [\mathrm{CH_3CHO}] \cdot \sum_{0}^{i} k_i^i[\mathrm{HB}_i] \qquad (2)$$

We also examined the decomposition of 3,3-dinitrobutan-2-ol in monochloroacetic and triethylamine buffers and methyl α-nitro-α-methyl- β-oxybutyrate decomposition in triethylamine buffers. In every case the rates showed a first-order dependence on nitro alcohol concentration.

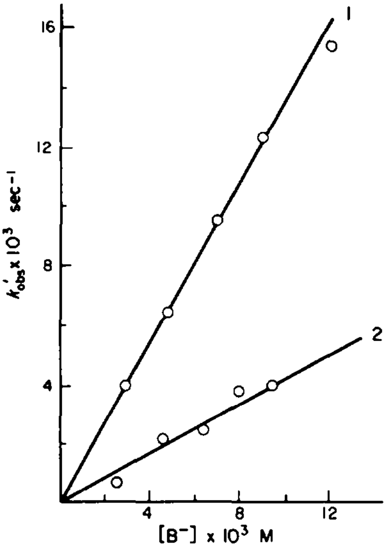


FIG 5. Plot of k'_{obs} for the 3,3-dinitrobutan-2-ol decomposition *vs* $[B^-]$. (1) triethylamine-triethylammonium perchlorate 1 : 1; (2) monochloroacetic acid-potassium monochloroacetate 1 : 1

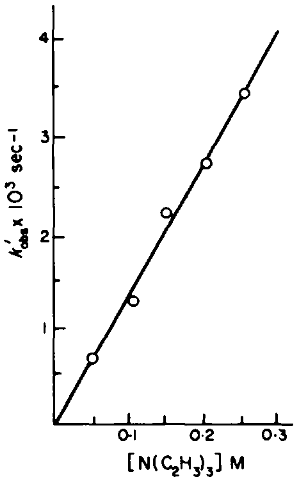


FIG 6. Plot of k'_{obs} for methyl-α-methyl-α-nitro-β-oxybutyrate decomposition *vs* $[B^-]$. Buffer: triethylamine-triethylammonium perchlorate 10 : 1

TABLE 1. RATE CONSTANTS FOR ACID CATALYSED NITRO ALCOHOL FORMATION AND BASE-CATALYSED NITRO ALCOHOL DECOMPOSITION

HB	pK_A^{HB}	1,1-Dinitroethane				Methyl α-nitropropionate			
		$k_1 M^{-2} sec^{-1}$		$k_{-1} M^{-1} sec^{-1}$		$k_1 M^{-2} sec^{-1}$		$k_1 M^{-1} sec^{-1}$	
		Experim.	calc.	Experim.	calc.	Experim.	calc.	Experim.	calc.
$Cl_2CHCOOH$	6,4	1,2 ± 0,1	—	$2,8 \cdot 10^{-3}$	$(2,4 \pm 0,6) \cdot 10^{-3}$	—	—	—	—
o-HOC_6H_4COOH	6,8[20]	0,8 ± 0,2	—	—	$(3 \pm 0,6) \cdot 10^{-3}$	—	—	—	—
$ClCH_2COOH$	9,0	—	0,6 ± 0,3	0,5 ± 0,1	—	—	—	—	—
$(C_2H_5)_3NH^+$	9,0[20]	—	1,5 ± 0,2	1,2 ± 0,2	—	—	75 ± 15	$(1,4 \pm 0,1) \cdot 10^{-2}$	—
$HOOC(CH_2)_2COOH$	9,6	0,3 ± 0,1	—	—	0,9 ± 0,4	—	—	—	—

In accordance with the principle of microscopic reversibility, bases should participate in the rate-limiting stage of the decomposition reaction. Plots of the observed pseudo-first order rate constants *vs* concentrations of "free" buffer bases are shown in Figs 5 and 6. From the slopes of these plots we obtained the values for the second-order rate constants for the reactions of the nitro alcohols with respective bases.

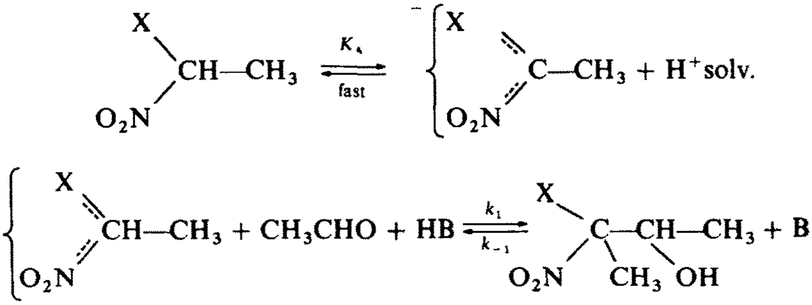
The values of the rate constants found for the formation and decomposition reactions of the nitro alcohols studied are given in Table 1.

DISCUSSION

Our data is in good agreement with the following mechanism of nitro alcohol formation in DMSO:

(a)

(b)



(3)

(c)

$$B^- + H^+\text{solv.} \underset{\text{fast}}{\overset{1/K_A^{HB}}{\rightleftharpoons}} HB$$

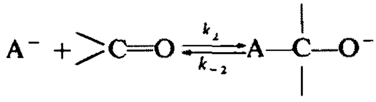
The equilibrium constant for the overall process: HA + $CH_3CHO \rightleftharpoons CH_3CHAOH$ can be expressed in the following way:

$$K^{HA}_{CH_3CHO} = \frac{K_A}{K_A^{HB}} \cdot \frac{k_1}{k_{-1}} \tag{4}$$

The applicability of this equation is confirmed by the data for 3,3-dinitrobutanol formation in dichloroacetate buffers where $K^{HA}_{CH_3CHO}$; k_1 and k_{-1} were determined independently. Table 1 shows that for carboxylic acids the k_1 value for a given compound anion increases as the HB acidity grows. The participation of acids in the rate-limiting stage of nitro paraffin-aldehyde condensation appears to be the first example of general acid catalysis of the carbanion addition to the CO group. A rough estimation gives a reasonable value for the Brönsted coefficient (0·2) for this catalysis. It seems probable that the reaction in question is also subject to general acid catalysis in water solution. The fact that it was not noticed previously[22,23] seems to be due to the large excess of water over other acidic components in the experimental conditions used and the comparatively low susceptibility of the reaction series to this catalysis.

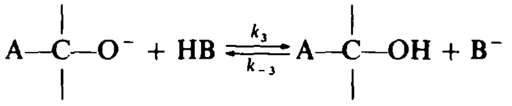
Trimolecular processes are usually considered as sequences of two bimolecular stages. For the reaction in question there are two probable schemes:

(a)



$$A^- + {>}C{=}O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A{-}\overset{|}{\underset{|}{C}}{-}O^-$$

(b)

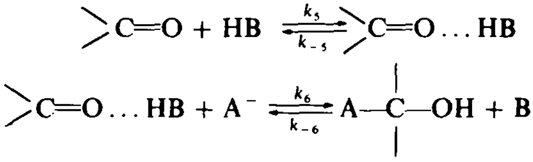


$$\mathrm{A{-}\overset{|}{\underset{|}{C}}{-}O^- + HB \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A{-}\overset{|}{\underset{|}{C}}{-}OH + B^-} \qquad (5)$$

and:

(a)

(b)



$$\mathrm{{>}C{=}O + HB \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} {>}C{=}O\ldots HB}$$

$$\mathrm{{>}C{=}O\ldots HB + A^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} A{-}\overset{|}{\underset{|}{C}}{-}OH + B^-} \qquad (6)$$

A consideration of the dependence of the third-order rate constant k_1 observed on the HB acidity enabled us to choose between them. Taking into account the fact that alcohols are very weak acids in DMSO,[24] one would expect a great difference between the pK_A-value of nitro alcohol and that of moderately acidic HB. The rate of proton transfer from HB to nitro alcohol O-anion should consequently be diffusion-controlled. Such a stage however can be rate-limiting, if the preceeding equilibrium is very unfavourable for nitro alcohol O-anion formation.[25] Then k_1 is equal to $k_3 \cdot k_2/k_{-2}$ and should not depend on HB acidity.

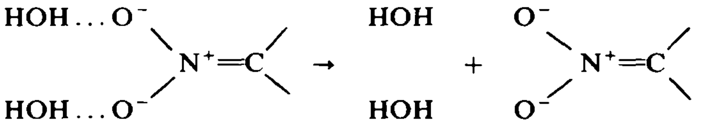
On the other hand, for scheme 6 k_1 equals $K' \cdot k_5$ where both K' (equilibrium constant for $>C{=}O\ldots HB$ formation) and k_5 depend on HB acidity. It was shown above that k_1 does depend on HB acidity. Thus, scheme 6 corresponds to the experimental facts, whereas scheme 5 does not.

The data obtained also gave us an opportunity to characterise the basicities and nucleophilicities of the carbanions studied towards the CO group. The respective values for DMSO and for water are given in Table 2.

Table 2 shows that there is a "normal" correlation of carbon basicities and carbon nucleophilicities for the two anions in DMSO. The 4,500-fold increase in basicity on going from the 1,1-dinitroethane anion to the methyl-α-nitropronate anion parallels the 50-fold increase in the nucleophilicity. The change from solvent DMSO to solvent water causes a levelling of the basicities (their ratio diminishes to 7·8) and an inversion of the nucleophilicities.

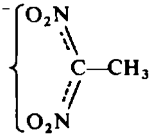
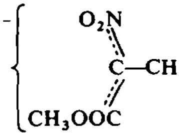
The levelling effect of protic solvents on anion basicities appears to be general[14, 26-28] and the specific solvation of anions by H-bonds seems to be the most likely cause of this phenomenon. The strength of the H-bonds grows with the increase in the "intrinsic" basicity of the anion, bringing about a levelling of the relative basicities of the solvated anions in protic media.

The inversion of nucleophilicities can be explained, if one assumes that chemical reactions are usually preceded by a solvent reorganization stage. This assumption was first formulated by Ogg and Polanyi[29] and Moelwyn-Hughes[30] and has recently been revived by Ritchie.[31-34] We believe that for ambident anions in various addition reactions to the C-atom this solvent reorganization can be visualized as follows:



(7)

TABLE 2. THE BASICITIES AND NUCLEOPHILICITIES OF THE TWO ANIONS STUDIED TOWARDS THE CO GROUP IN DMSO AND IN WATER

Anion	DMSO		H₂O	
	K_{bas}^{DMSO*}	$k_1^{HN^+(C_2H_5)_3}$	$K_{bas}^{H_2O*}$	$k_1^{H_2O}$
	M^{-2}	$M^{-2}\,sec^{-1}$	M^{-2}	$M^{-1}\,sec^{-1}$
	$1{\cdot}2 . 10^9$	1·5	$5{\cdot}2† . 10^6$	0·463
	$5400 . 10^9$	75	$38{\cdot}4 . 10^6$	0·196†

* Equilibrium constant for the reactions:

$$A^- + CH_3CHO + H^+_{solv} \rightleftarrows RCH(A)OH$$

$$K_{bas} = \frac{K^{HA}_{CH_3CHO}}{K_A};$$

pK_A^{DMSO}: for 1,1-dinitroethane 6·6[14]: for methyl-α-nitroproprianate 10·5[14].

† Calculated using data.[15]

The H-bonds between the ambident anion and the protic solvent enhance the fixation of the maximum electron density on the O atoms. It seems reasonable that the shift of electron density from O to C during the attack of the carbonion on an electrophile should involve the preliminary breakdown of these H-bonds.

Fig 7 shows the free-energy profile suggested for the nucleophilic addition of two

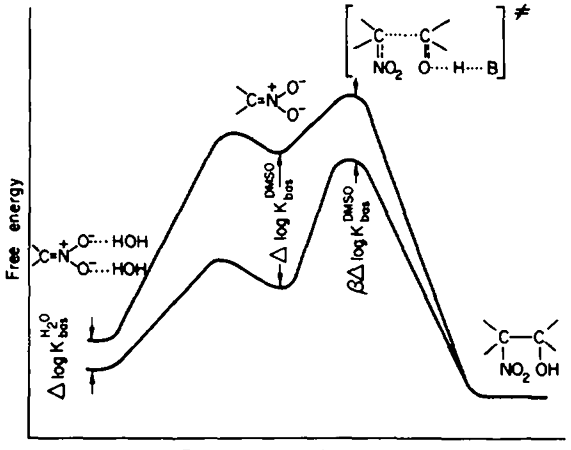


FIG 7. The free-energy profile of nucleophilic addition suggested for two ambident anions in water

ambident anions in water which includes this preliminary desolvation stage. In the initial reagent state the difference between the free energies of the two anions is equal to $\Delta \lg K_{bas}^{H_2O}$. This difference should be much greater for the desolvated anions, due to the absence of the levelling effect of the H-bonds. The $\Delta \lg K_{bas}^{DMSO}$ may serve to show this difference and, consequently, the difference between the free energies of the respective transition states should be $\beta \Delta \lg K_{bas}^{DMSO}$ where $0 < \beta < 1$.

Provided that $\beta \Delta \lg K_{bas}^{DMSO}$ is greater than $\Delta \lg K_{bas}^{H_2O}$ the effective activation free energy for the more basic anion is greater than that for the less basic one which results in the inversion of the nucleophilicities of the two anions. It follows that in a dipolar aprotic medium the correlation of basicities and nucleophilicities should be "normal" which is in fact the case.

A rough estimation of the β-value from the data for 1,1-dinitroethane and methyl α-nitropropionate anions in DMSO suggests a value of 0·53.

Assuming that the relative stabilities of desolvated anions are reflected in the transition states, it seems reasonable to expect a linear logarithmic relationship with a slope of 0·53 between the rates of the OH^--catalysed decomposition of nitro alcohols in water and the basicities of the corresponding nitro compound anions in DMSO. The data for nitro alcohols obtained from acetaldehyde and various nitro compounds corresponds satisfactorily to a line of slope 0·5 (Fig 8).

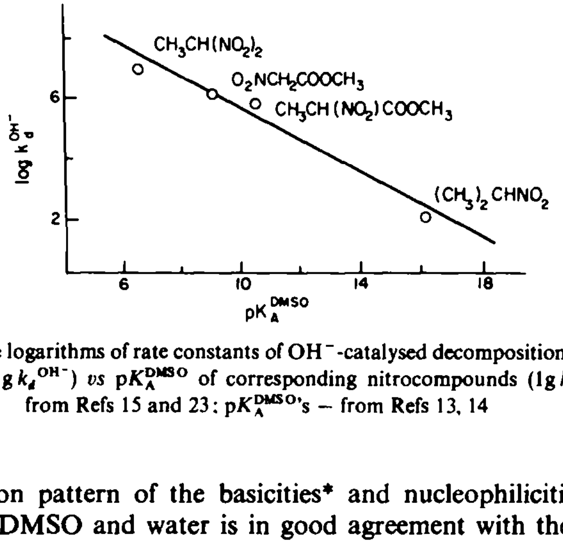


FIG 8. The plot of the logarithms of rate constants of OH^--catalysed decomposition of nitro alcohols in water ($\lg k_d^{OH^-}$) *vs* pK_A^{DMSO} of corresponding nitrocompounds ($\lg k_d^{OH^-}$ – from Refs 15 and 23: pK_A^{DMSO}'s – from Refs 13, 14

Thus, the correlation pattern of the basicities* and nucleophilicities for nitro compound anions in DMSO and water is in good agreement with the concept of the preliminary anion desolvation stage in protic media.

It seems logical to suggest that it might also prove to be useful in understanding ambident anion reactivity towards the hydrogen electrophilic centre. For the free energy barrier of proton-transfer reaction Marcus[35] suggested the equation 8 which is formally analogous to the theoretical one for electron-transfers.

$$\Delta F^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta F^0}{\lambda}\right) \tag{8}$$

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* The use of hydrogen basicities instead of carbon basicities is justified, since one is directly proportional to the other for the anions is question.[7]

where: ΔF^0—"standard" free energy of the reaction

λ—energy of the "structural reorganization" which can be both intramolecular and solvational.

Hence the free-energy barrier of the reaction:

$$R^- + HB \xrightarrow{k_R} RH + B^- \tag{9}$$

at $pK_A^{HB} = pK_A^{RH}$ (e.g. $\Delta F^0 = 0$) is determined only by the "structural reorganization" of R^- and BH. When HB and HR are acids of the O–H (or N–H) type the rates of processes 9 are usually close to those of diffusion and consequently the "structural reorganization" of O–H (or N–H) acids and bases is negligible.[35] On the other hand the protonation of carbanions by O–H or N–H acids is often very slow which shows that "structural reorganization" of carbanions is important.

The parameters of the Brönsted relationship (G_{HB} and α) between the rates of protonation and the acidities of O–H or N–H type proton-donors are known for some ambident carbanions:

$$\frac{1}{p}k_R = G_{HB}\left(\frac{q}{p}\cdot K_A\right)^{\alpha} \tag{10}$$

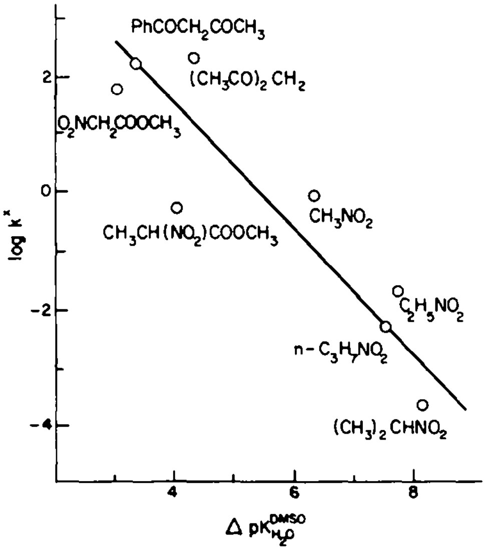

Fig 9. Plot of lg k^x vs $\Delta pK^{DMSO}_{H_2O}$.

The data for this plot were taken from the references given below.

	lg k^x	$pK^{DMSO}_{H_2O}$
Benzoylacetone	(36, 37)	(28)
Acetylacetone	(36, 37)	(28)
Nitromethane	(39)	(13)
Nitroethane	(39)	(13)
1-nitropropane	(40)	(13)
2-nitropropane	(41)	(13)
Methyl-α-nitro-propionate	(42)	(14)
Methyl nitroacetate	(43)	(14)

We denote as k^x the k_R value at $K_A^{HB} = K_A^{RH}$. Lg k^x is obviously a measure of the "structural reorganization" of the carbanion R^-. In order to elucidate the extent to which the protic solvent reorganization affects the overall "structural reorganization", we plotted the calculated lg k^x values *vs* $\Delta pK_{H_2O}^{DMSO} = pK_A^{DMSO} - pK_A^{H_2O}$ which stands quantitatively for the relative efficiency of the formation of H-bonds between water and the corresponding carbanions (Fig 9).

There is a rough correlation (r = 0·90) between these two values and slope 1. Hence, the "structural reorganization" of the carbanions in protonation reactions in water is mainly determined by breaking their H-bonds with the solvent. We have not taken into account the intramolecular reorganization and the steric effects. An interplay of these factors may be responsible for the considerable deviations of some points from the straight line in Fig 9.

The results reported in this article suggest that the specific solvation of ambident anions by H-bonds is one of the most important factors affecting their nucleophilicity and is responsible for their anomalous behaviour in protic media.

EXPERIMENTAL

Materials. DMSO "ch" (pure) grade reagent was purified by the method described.[32] 3,3-Dinitrobutan-2-ol was synthesised from 1,1-dinitroethane and acetaldehyde,[23] b.p. 55° (at 0·5 mm), $n_D{}^{25}$ 1·4081. Methyl α-nitro- α-methyl-β-oxybutyrate was prepared from methyl-α-nitropropionate and acetaldehyde[44] b.p. 74–75° (at 1·5 mm), n_D^{25} 1·4500. 1,1-Dinitroethane[45] was obtained, n_D^{20} 1·4340; lit.[45] n_D^{20} 1·4341–1·4346. Methyl-α-nitropropionate was prepared from methyl-α-bromopropinate and $NaNO_2$,[46] b.p. 58° (at 1·5 mm), n_D^{20} = 1·4212; lit. n_D^{20} 1·4209.[46] Dichloroacetic acid "ch" grade reagent was distilled in a vacuum. Succinic acid "ch" grade reagent was recrystallized from water. Salicylic acid was three times recrystallized from water. The potassium salts of the three acids mentioned above were prepared by mixing equivalent amounts of KOH and corresponding acids in EtOH and recrystallizing from suitable solvents. Tetraethylammonium methylate[47] was added to an equivalent amount of dichloroacetic acid in MeOH. The solvent was then avaporated in a vacuum and the residue was recrystallized from anhyd EtOAC. Potentiometric titration of the product with picric acid in DMSO showed it to be 98% pure tetraethylammonium dichloroacetate. Triethylamine was purified by method in Ref. 48.

After mixing the equivalent amounts of triethylamine and perchloric acid in EtOH, the solvent was evaporated in a vacuum and the triethylammonium perchlorate was dried in a vacuum over P_2O_5. Tetraethylammonium perchlorate was prepared by method in Ref. 49. Acetaldehyde solutions in DMSO were prepared by weight, using acetaldehyde freshly distilled under argon.

Measurements. The potentiometric measurements were carried out using a titrigraph "Radiometer TTT-lc (SBU-la)SBR-2c and spectrophotometric ones—on a Hitachi EPS-3 instrument.

All measurements of the equilibria and kinetics of nitroalcohol formation and decomposition were carried out at 25° and a constant ionic strength of 0·05 in DMSO (tetraethylammonium perchlorate) and 0·1 in H_2O (KCl) was used.

Acidity constants in DMSO. The pK_A-value for dichloroacetic acid was determined by potentiometric titration of its tetraethylammonium salt with picric acid in DMSO and was found to be 6·4 ± 0·1. The homoconjunction constant ($K_{HB_2^-}$) was calculated[50] and was found to be 60 ± 30 M^{-1}. A Radiometer G-20IB glass electrode was used for all emf measurements. The reference cell consisted of a silver electrode immersed in a 0·01 M $AgNO_3$ in DMSO. The glass electrode cell was connected to the reference cell by a salt bridge which consisted of a polyethylene tube filled with a 0·05 M tetraethylammonium perchlorate in DMSO. The "concentration" dissociation constants of $ClCH_2COOH$ and $(CH_2COOH)_2$ were obtained by the spectrophotometer method, using methyl-α-nitropropionate (pK_A^{DMSO} = 10·5[14] as an indicator, and extrapolated to zero ionic strength. We found pK_A = 9·0 for $ClCH_2COOH$ and 9·6 for $(CH_2COOH)_2$ (the first dissociation step).

The equilibrium constants ($K_{CH_3CHO}^{HA}$). Acetaldehyde was added to buffer solns containing a partially

(20–50%) dissociated nitro compound. This mixture was placed in the sample cell of the spectrophotometer, the reference cell being filled with a soln containing the same amounts of these ingredients except for the nitro compound. The optical density at the absorbance maximum of the nitro compound anion gradually decreased and finally reached an equilibrium value.

$K^{HA}_{CH_3CHO}$ was calculated from the equation:

$$K^{HA}_{CH_3CHO} = \frac{\{\Delta D + E_{app}[CH_3CHAOH]_0\} \cdot E_{app}}{\left(1 - \frac{E_{app}}{E_{A^-}}\right)\{E_{app}[HA]_0 - \Delta D\}\{E_{app}[CH_3CHO]_0 - \Delta D\}}$$

where: ΔD—the decrease in optical density.

E_{app}—apparent extinction coefficient of the nitrocompound in the buffer.

E_{A^-} —the extinction coefficient of the nitro compound anion in DMSO.

$[HA]_0$; $[CH_3CHO]_0$; $[CH_3CHAOH]_0$—initial concentrations of the respective species.

The results are summarized in Tables 2 and 3.

TABLE 3. $K^{HA}_{CH_3CHO}$ FOR 1,1-DINITROETHANE IN DMSO BUFFER: $Cl_2CHCOOH$—$Cl_2CHCOOK$ 1:1

Expt.	Initial concentrations M			$K^{HA}_{CH_3CHO}$ M^{-1}
	$[HA] . 10^4$	$[CH\ CHO] . 10^2$	$[CH_3CHAOH] . 10^4$	
1	0·989	0·993	—	284
2	0·928	1·242	—	261
3	1·140	0·381	—	208
4	1·059	0·709	—	299
5	4·032	4·83	3·66	422
6	3·769	6·83	3·57	388
7	3·533	8·58	3·44	386
8	3·194	1·02	3·31	300

Average: 300 ± 70

TABLE 4. $K^{HA}_{CH_3CHO}$ FOR METHYL-α-NITROPROPIONATE IN DMSO BUFFER: $HOOCCH_2CH_2COOH$—$HOOCCH_2CH_2COOK$ 1:5

Expt.	Initial concentrations M		$K^{HA}_{CH_3CHO}$ M^{-1}
	$[HA] . 10^4$	$[CH_3CHO] . 10^2$	
1	0·621	2·61	167
2	0·664	1·86	174
3	0·714	1·10	174
4	0·582	3·28	163
5	0·710	0·942	180
6	0·660	1·75	144
7	0·570	3·07	145

Average: 170 ± 20

K^{HA}_{CH3CHO} for methyl-α-nitropropionate in water was determined by the potentiometer technique. Known amounts of acetaldehyde were added to solutions containing methyl-α-nitropropionate and its potassium salt. The pH of the solution increased during the reaction.

$$K^{HA}_{CH_3CHO} = \frac{n(n-1)}{n\{[CH_3CHO]_0 - [HA]_0\} + [HA_0]}(K_{hyd} + 1)$$

where $n = \text{antilog}\,(\text{pH}_2^{-}\,\text{pH}_1)$; pH_1—initial pH-value; pH_2—equilibrium pH-value; $K_{\text{hyd}} = 0{\cdot}92$ (51)—the hydration constant of acetaldehyde. The results of these calculations are shown in Table 4.

TABLE 5. $K^{\text{HA}}_{\text{CH}_3\text{CHO}}$ FOR METHYL-α-NITROPROPIONATE IN WATER

Expt.	Initial concentration M		$K^{\text{HA}}_{\text{CH}_3\text{CHO}}$ M^{-1}
	$[\text{HA}].10^2$	$[\text{CH}_3\text{CHO}].10^2$	
1	0·825	0·77	16·7
2	0·776	1·44	15·4
3	0·718	2·15	14·8
4	0·86	1·20	14·4
5	0·843	2·40	16·1
6	0·8	3·89	15·2
7	0·77	6·33	12·3
			Average: 15·4 ± 2

Kinetic measurements. The kinetics of the formation or decomposition of nitro alcohols were followed by recording the change in the optical density of solns at the absorption maxima of the respective anions. Acetaldehyde and buffer components were always in more than 30-fold excess over nitro compounds.

Under the experimental conditions used both the formation of nitro alcohols and their decomposition were essentially irreversible. A typical kinetic run is described below.

Two 10 ml amounts of 0·453N CH_3CHO soln in dicloroacetate buffer solution ($\text{Cl}_2\text{CH}_2\text{COOH}$ 0·05N —$\text{Cl}_2\text{CH}_2\text{COOK}$ 0·05N) were placed in two flasks. 0·458 ml of the pure buffer was added to one of the amounts and 0·458 ml of $2{\cdot}3 \cdot 10^{-3}$N soln of 1,1-dinitroethane in the same buffer to the other. The former was placed in the reference cell and the latter in the sample cell. The decrease in optical density was recorded.

Kinetic curves were treated using a simple first-order equation:

$$\lg \frac{D_\infty - D_0}{D_\infty - D_r} = \frac{1}{2{\cdot}3} k_{\text{obs}}\,\tau$$

3,3-*dinitrobutan-2-ol decomposition in dichloroacetic buffers* is very slow. Its kinetics were studied in conditions of the pseudo-zero order.

The second-order rate constant was calculated from the equation:

$$k_{-1}^{\text{Cl}_2\text{CHCOO}^-} = \frac{\Delta D}{E_{\text{app}}\,\Delta\tau[\text{CH}_3\text{CHAOH}]\cdot l\cdot[\text{Cl}_2\text{CH}\,\text{COO}^-]}$$

where: ΔD—the increase in optical density with time; $l = 1$ cm the cell's width.

The value $2{\cdot}48 \cdot 10^{-3}\ \text{M}^{-1}\ \text{sec}^{-1}$ was obtained.

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