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Kinetic and Equilibrium Acidities of Nitrocycloalkanes

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Rates of deprotonation by lyate ion in 50% (v/v) MeOH–H_2O were determined for C_3–C_8 and C_{12} nitrocycloalkanes. Equilibrium acidities in this solvent were also determined for C_4–C_8 and C_{12} nitrocycloalkanes and were determined in Me_2SO for C_3–C_7 nitrocycloalkanes. Equilibrium acidities in the two solvents showed a remarkable similarity in their variation with ring size, despite a (constant) difference of 7.75 pK units in the acidity constants. The equilibrium acidity of nitrocyclopropane was found to be over 10^8 times smaller than that for nitrocyclobutane, and its kinetic acidity in water was found to be over 10^3 times smaller. The correspondence in the relative order of equilibrium and kinetic acidities between the C_8 and the C_4 nitrocycloalkanes is contrasted with the lack of correspondence between the equilibrium and kinetic acidities of the C_4 and the C_5 nitrocycloalkanes. This is explained by assuming a different mechanism for deprotonation of nitrocyclopropane as compared to other nitroalkanes.

In the preceding paper we discussed the "anomalous" Brønsted coefficients observed for the deprotonation of acyclic nitroalkanes in protic solvents. A lack of the "expected" correlation between kinetic and equilibrium acidities of certain nitrocycloalkanes has also been apparent for some time.[2,3] The relative rates of deprotonation for nitrocycloalkanes by hydroxide ion in water and by lyate ion in a variety of other protic solvents has been found to vary with ring size in the order: $4 > 5 > 7 > 8 > 6 \gg 3$.[3] (Nitrocyclopropane failed to react.) In contrast, the order of equilibrium acidities in 33% (w/w) MeOH–H_2O for nitrocycloalkanes was found to vary with ring size in the order: $8 > 7 > 5 > 6 > 4 \gg 3$.[3] (The acidity constant for nitrocyclopropane was too small to measure.) Studies of kinetic and equilibrium acidities of nitrocycloalkanes in 50% (v/v) MeOH–H_2O were in progress at the time these data were published. The work was continued, since it seemed worthwhile to obtain kinetic and equilibrium measurements in the same solvent.[4] The equilibrium acidity studies have now been extended to dimethyl sulfoxide (Me_2SO) solution, and rate and equilibrium data for nitrocyclopropane have been obtained.

Results

Equilibrium Acidities for Nitrocycloalkanes. The relative values for the equilibrium acidities obtained potentiometrically in 50% (v/v) MeOH–H_2O (Table I) agreed reasonably well with those determined conductometrically in 33% (w/w) MeOH–H_2O,[3] except for nitrocyclohexane, for which a higher relative value was found. Repetition of this measurement in 33% (w/w) MeOH–H_2O gave, in our hands, a pK of 9.58, instead of the value reported (8.92). (On the other hand, we were able to check the values reported for nitrocyclopentane and nitrocycloheptane in 33% MeOH–H_2O to within 0.1 pK unit.) The value of 9.58 appears to be correct, since it places the pK of nitrocyclohexane within a few tenths of a unit of that reported for nitrocyclobutane (pK = 9.53),[3] and we have observed a close correspondence between the pK's for these two nitrocycloalkanes in: (a) water (8.56 and

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Table I. Equilibrium Acidities of Nitrocycloalkanes in 50% (v/v) MeOH-HOH and in Dimethyl Sulfoxide (Me_2SO) at 25 °C

registry no.	ring size	pK (50% MeOH–HOH)[a]	pK (Me_2SO)[b]
13021-02-8	3	>18[c]	26.9 ± 0.2[d]
2625-41-4	4	10.05 ± 0.03	17.82 ± 0.05
2562-38-1	5	8.15 ± 0.02	16.00 ± 0.05
1122-60-7	6	10.07 ± 0.01	17.90 ± 0.05
2562-40-5	7	8.15 ± 0.01	15.80 ± 0.05
24509-62-4	8	7.37 ± 0.03	
1781-70-0	12	9.6 ± 0.1[e]	
79-46-9	Me_2CHNO_2	8.85 ± 0.02	16.89 ± 0.05
551-88-2	Et_2CHNO_2	10.17 ± 0.03	

[a] Determined potentiometrically. [b] Determined by the indicator method described by W. S. Matthews et al., *J. Am. Chem. Soc.*, **97**, 7006 (1975). [c] Based on the absence of UV absorption typical of $>C{=}NO_2^-$ in 1 M aqueous NaOH. [d] Decomposition occurs. [e] Extrapolated from data in 75% (v/v) MeOH–H_2O.

Table II. Rates of Deprotonation of Nitroalkanes by Lyate Ion in 50% (v/v) MeOH–H_2O (k_2) at 25 °C

ring size	k_2, $M^{-1}\ s^{-1}$ [a]	k_2 rel	k_{-2} rel[b]
3	0.002[c]	0.0072	~10^5
4	5.4	19	18
5	1.4	5	0.059
6	0.28	(1.0)	(1.0)
7	0.87	3.1	0.037
8	0.65	2.3	0.0045
12	0.13	0.46	0.15
Me_2CHNO_2	0.26	0.93	0.055

[a] Determined spectrophotometrically unless otherwise noted; the reproducibility of runs was better than ±5%. [b] Relative rate of protonation of $C{=}NO_2^-$ on carbon calculated from the equation $k'_{-2}/k_{-2} = K_{HA}k'_2/K'_{HA}k_2$. [c] Rate of deuterium exchange catalyzed by DO^- in D_2O; reproducible to ±5%. The rate for *trans*-2-methyl-1-nitrocyclopropane was the same, within experimental error, while that for the cis isomer was about tenfold faster.

8.61); (b) 50% (v/v) MeOH–H_2O (10.05 and 10.07); and (c) 50% (v/v) dioxane–H_2O (10.88 and 11.16). Our value for nitrocyclohexane in water is 0.3 pK unit above that reported in another investigation,[5] but agrees with a value we have extrapolated into water from measurements in aqueous dioxane (using 50, 40, 25, and 10% of dioxane).[4]

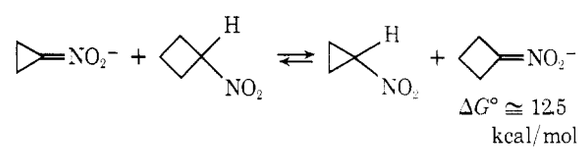
Comparison of the equilibrium acidities in Me_2SO with those in 50% MeOH–HOH for the C_4–C_7 nitrocycloalkanes shows that they differ by an almost constant amount (7.75 ± 0.1 pK unit). Acyclic nitroalkanes show a similar behavior, but the differences are not quite so constant.[6a,b]

Contrary to the report that *trans*-2-ethylnitrocyclopropane fails to undergo base-catalyzed deuterium exchange even under strenuous conditions,[3] we found that nitrocyclopropane (and *cis*- or *trans*-2-methylnitrocyclopropanes) underwent deuterium exchange readily with either 0.1 N NaOD–D_2O or 0.1 N lyate ion in 50% (v/v) MeOD–D_2O. The rate of deprotonation for nitrocyclopropane is over 100 times slower than that of nitrocyclohexane or an open-chain analogue, 2-nitropropane, however, and is over 2500 times slower than that of nitrocyclobutane (Table II). For deuterioxide exchange of the protio compound in D_2O, $\Delta H^{\ddagger}$ is 13 ± 1 kcal/mol, which is the same as that of nitrocyclohexane in 50% dioxane–water;[3] $\Delta S^{\ddagger}$ for deprotonation of nitrocyclopropane is, however, −27 ± 2 eu, a value much lower than that reported for nitrocyclohexane (−14.5 eu).[3]

In comparing the deuterium exchange rates for nitrocyclopropane with the rates for appearance of the nitronate ions (determined spectrophotometrically) for the other nitrocycloalkanes, one must consider the possibility that the rate of deuterium exchange is complicated by internal return.[7] This does not appear to be a major factor, judging from "mixed" kinetic isotope effect, $k_{H(D_2O)}/k_{D(H_2O)}$, of 9.1 observed for nitrocyclopropane. The "mixed" isotope effect is the product of the "normal" substrate isotope effect, k_H/k_D (both in H_2O), and the solvent isotope effect (k_{D_2O}/k_{H_2O}) (both with the protio compound). For 2-nitropropane, the "normal" isotope effect has been found to be 7.6 ± 0.2, and k_{D_2O}/k_{H_2O} has been found to be 1.36.[8] Solvent isotope effects for carbon acids generally fall in the range 1.2–1.6.[9] Judging from these data, the k_H/k_D isotope effect for nitrocyclopropane in water at 25 °C will be about 6.5, which would appear to rule out internal return as a major factor.

Discussion

Variation of Equilibrium Acidities of Nitrocycloalkanes with Ring Size. Examination of Table I shows that the relative order of equilibrium acidities observed in protic solvents for nitrocycloalkanes, namely, 5, 7 > 4, 6 ≫ 3, is observed also in Me_2SO solution. The changes in equilibrium position with changes in ring size are evidently independent of solvent and depend only on the nature of the ring. The changes in these equilibrium constants for the C_4–C_8 and C_{12} ring sizes in 50% MeOH–H_2O are in the same order as the equilibrium constants for formation of ketones from cyanohydrins in 95% EtOH, namely, $C_4 < C_5 > C_6 < C_7 < C_8 > C_{12} \simeq R_2C{=}O$.[10] The major effects determining the position of the cyanohydrin equilibria are believed to be angle strain in the C_4 compound and torsional strains in the C_5, C_7, and C_8 compounds.[10] Adopting this analysis, the unfavorable dissociation constant for nitrocyclobutane, relative to C_5, C_7, and C_8 nitrocycloalkanes (Table I), can be explained by assuming that angle strain in the C_4 nitronate ion overshadows torsional strain in the C_4 nitroalkane. Similarly, the remarkably low dissociation constant for nitrocyclopropane (9 pK units lower than nitrocyclobutane in Me_2SO) can be attributed largely to strain in the C_3 nitronate ion. Introduction of one trigonal center into cyclopropane has been estimated to increase the total strain energy by 13 kcal/mol, as compared to only about 1 kcal/mol for cyclobutane.[11]



$\Delta G^{\circ} \cong 12.5$ kcal/mol

The greater degree of dissociation of the C_5, C_7, and C_8 nitrocycloalkanes as compared to the C_6 or C_{12} nitrocycloalkanes (Table I) can be attributed to the presence of torsional strains in the nitrocycloalkanes, which are partially relieved in forming the corresponding nitronate ions.[10]

Comparison of Equilibrium and Kinetic Acidities for Nitrocycloalkanes. The rates of deprotonation of nitrocycloalkanes by lyate ion in protic solvents follow the relative order 4 > 5 > 7, 8 > 6, 12, acyclic ≫ 3 (see Table I and ref 3). (The reversal in the order of the relative rates and equilibrium constants for the C_4 and C_5 nitrocycloalkanes has been commented on earlier as an example of an anomalous Brønsted relationship.[2]) The relative order of kinetic acidities of the C_4, C_5, and C_6 nitrocycloalkanes obtained in this way are 19: 5.0:1.0, which corresponds closely to the relative order of kinetic acidities of cycloalkanes determined by cesium cyclohex-

ylamide catalyzed tritium exchange in cyclohexylamine, CHA (28:5.7:1.0).[12] The similarity in these rate patterns may seem surprising when one considers that, although the rate-limiting step is presumably formation of a carbanion in each reaction, in one instance carbanion formation is a highly endoenergetic reaction, whereas in the other it is an exoenergetic reaction (formation of a nitronate ion). In the preceding paper in this series we pointed out, however, that as a *general rule,* rates of deprotonation of acyclic nitroalkanes are *not* governed by nitronate ion stabilities.[6c] The failure of the strain in the (developing) cyclobutane nitronate ion to produce an observable increase in transition state energy is therefore consistent with this general pattern of behavior.[6c] This result can be rationalized by assuming a reactant-like transition state, but this is not consistent with the large k_H/k_D isotope ratios observed; k_H/k_D = 8.4 for nitrocyclobutane, 8.3 for nitrocyclopentane, and 8.8 for nitrocyclohexane in aqueous dioxane.[3] For this reason we favor a mechanism involving the formation, in the rate-limiting step, of an essentially pyramidal, singly H-bonded intermediate (**2** in this instance).[6c]

1 2 3

According to this mechanism the rate-limiting step is the (endoenergetic) conversion of **1** to **2.** The extent of H–C bond breaking can be appreciable (large k_H/k_D) and some relief of torsional strain can occur (leading to rate acceleration for deprotonation of nitrocyclobutane relative to nitrocyclopentane) without much increase in angle strain. (See Figure 4 in ref 6c and the accompanying discussion for more details.)

The rates of protonation of the nitronate ions on carbon by MeOH–H_2O solvent (k_{-2}^{rel}) can be calculated from the deprotonation rates and the equilibrium constants (Table II). The order observed, C_4, $C_6 > C_5$, C_7, is similar to that for the rate of reduction of the corresponding cycloalkanones by sodium borohydride,[13a] and follows Brown's rule[13b] that the ease of transformation of sp^2 to sp^3 carbon atoms in carbocyclic ring systems is greater for four- an six-membered rings than for five- and seven-membered rings.[14] If we assume that this order of rates holds also for protonation on carbon by the conjugate acids of the solvent, it would account for the relative orders of equilibrium acidities observed; the protonation rates rather than the deprotonation rates would then control the relative equilibrium acidities.

The rate pattern for deprotonation of nitrocycloalkanes with 7, 8, and 12 members, i.e., 7 > 8 > 12 (Table II), is also the same as that for cycloalkanes,[12] although the order of rates relative to the six-membered ring compound differ slightly in the two systems. The mechanism outlined for deprotonation of nitrocyclobutane, i.e., **1 → 2 → 3,** appears appropriate also for these nitrocycloalkanes. On the other hand, the rate of deprotonation for nitrocyclopropane, relative to the rates for other nitroalkanes, shows an opposite behavior from that for the rate for cyclopropane, relative to the rates for other cycloalkanes.

Cyclopropane is deprotonated by cesium cyclohexylamide in CHA at a rate about 2500 times faster than is cyclobutane.[12] These rates, as well as those for C_5–C_8 cycloalkanes, correlate linearly with ^{13}C–H NMR coupling constants, which indicates that the amount of s character in the C–H bond is the dominant factor controlling cycloalkane kinetic acidities.[12,15] Theoretical calculations also indicate that the C–H bond in cyclopropane has appreciably more s character than do the C–H bonds in higher cycloalkanes.[16] Apparently this factor is overshadowed completely in determining the kinetic acidity of the H–C bonds in nitrocyclopropane, since it is deprotonated in protic solvents at a rate about 2500 times *slower* than is nitrocyclobutane (Table II). Remarkably enough, the major part of the rate difference appears to be in the $\Delta S^{\ddagger}$ term, judging from the comparison of the activation parameters made in the Results. These data suggest a mechanistic change for deprotonation of nitrocyclopropane as compared to other nitroalkanes. The deprotonation of nitrocyclopropane is uphill, as compared to other nitrocycloalkanes and acyclic nitroalkanes, by at least 11 kcal/mol. It has been suggested by Albery that in exoenergetic reactions, such as the deprotonation of C_4–C_8 nitrocycloalkanes by hydroxide ion, the major part of solvent reorganization may follow C–H bond breaking as in the mechanism shown for conversion of **1** to **3.**[17] However, for endoenergetic reactions, such as deprotonation of nitrocyclopropane by hydroxide ion, solvent reorganization may accompany C—H bond breaking. This would account for the unusually large negative $\Delta S^{\ddagger}$ for deprotonation of nitrocyclopropane. In terms of the mechanism shown, it could mean that nitrocyclopropane is converted directly to its nitronate ion in the rate-limiting step without intervention of an intermediate analogous to **2.** In this transition state the large strain energy in the (developing) C_3 nitronate ion can provide a strong destabilizing effect. The rate of base-catalyzed deuterium exchange for nitrocyclopropane, as compared to the rate of deprotonation of nitrocyclobutane, is 6×10^6 slower than expected on the basis of the relative rates of base-catalyzed deuterium exchange of the C_3 vs. the C_4 cycloalkane. The 12 kcal/mol greater strain in the C_3 vs. the C_4 nitronate ion, which corresponds to a rate ratio of about 10^9, is sufficient to account for this.

Experimental Section

Reagents. Partially aqueous solvents were prepared by combining measured volumes of water and either methanol or dioxane to achieve the desired volume/volume percentage composition. Reagent-grade dioxane was refluxed with molten sodium for at least 24 h and then distilled. Baker and Adamson reagent-grade (ACS Code 1212) absolute methanol was used without further purification. Sodium hydroxide solutions were either standardized against Banco Standardized or Fischer Certified standard hydrochloric acid to a phenolphthalein end point or prepared from Anachemia Acculute solutions. The basic solutions in mixed solvents were prepared by combining appropriate volumes of aqueous sodium hydroxide and the organic component and diluting with mixed solvent to the desired volume.

Kinetic Procedure. The rates of deprotonation from the nitroalkanes by lyate ion in 50% (v/v) aqueous methanol at 15 °C, other than nitrocyclopropane, were determined spectrophotometrically by following the appearance of the nitronate ion absorption in the ultraviolet region (λ_{max} 225–245 nm: ϵ_{max} 9000–14000), as previously described.[18] The measurements were performed either on the Cary Model 15 or the Beckman Kintrac VII recording spectrophotometers. When a clear infinity value could not be obtained experimentally due to decomposition or side reactions, infinity absorbances were calculated by a Kezdy treatment of the data obtained over 3–4 half lives.[19]

Deuterium exchange rates for nitrocyclopropanes were determined using 5–10-mg aliquots in 4-mL vials containing 3 mL of ~1 M NaOD/D_2O. After shaking to promote dissolution, the vials were allowed to remain in a constant temperature bath for appropriate times. For analysis, the contents of the vial was extracted with 0.5 mL of carbon tetrachloride, and the ratio of the peak areas for the α proton (δ 3.9–4.4) and the β protons (δ 0.5–2.5) were determined by NMR. Rate constants were determined from the equation, $\ln [A - A_\infty] = kt$, where A is the ratio at time t. The accuracy of the method is limited by the low solubility of nitrocyclopropane (~5–10 mg/mL of D_2O), and the rates are probably accurate to no better than ±10%. For nitrocyclopropane in D_2O k at 25 °C was 3.9×10^{-3} M^{-1} s^{-1}, and for nitrocyclopropane-d_1 in H_2O k at 25 °C was 0.43×10^{-3} M^{-1} s^{-1}. The rate constant for *trans*-2-methyl-1-nitrocyclopropane in D_2 was identical, within experimental error, to that for nitrocyclopropane itself. For *cis*-2-methyl-1-nitrocyclopropane in D_2O k at 25 °C was ~4×10^{-3} M^{-1} s^{-1}.

Rate constants for nitrocyclopropane in D_2O were determined at

15 and 35 °C by monitoring the appearance of the OH peak in the solvent by NMR. For this purpose 100 mg of nitrocyclopropane was placed in an NMR tube and 0.5 mL of ~1 M NaOD/D_2O added. After making sure that in a 2-h trial run that the OH peak (δ 4.8) was not saturated at 60 Hz paper width and 200-s scan, fresh samples were used to scan the OH peak as a function of time. Peak areas were determined by cut-and-weigh, and the data analyzed as first-order kinetics.

Materials. Nitrocyclohexane was obtained as a gift from the Commercial Solvents Corp. and nitrocyclooctane was obtained as a gift from Professor J. G. Traynham. Other nitrocycloalkanes, except for nitrocyclopropane, were prepared by the oxidation of the keto oximes as described previously.[6] Nitrocyclopropane was prepared by the method of Lampman, Horne, and Hager[20] and purified by GLC using a ⅜ in. × 10 ft Carbowax on acid-washed Chromosorb W column at 110 °C and 160 mL/min flow rate to give a clear liquid: n^{23}_D 1.4380 [lit.[20] n^{20}_D 1.4395]; NMR ($CDCl_3$) δ 1.10 (m, 2 H), 1.60 (m, 2 H), 4.33 (m, 1 H); IR (film) 1540, 1370 cm^{-1}. 2-Methyl-1-nitrocyclopropane was prepared in a similar manner starting from 1,3-dibromobutane. GLC analysis indicated the presence of two isomers in a ratio of 10:1. Isolation of each was accomplished by preparative GLC using a ¼ in. × 20 ft 3% Carbowax on acid-washed Chromosorb W column at 80 °C and a flow rate of 80 mL/min. The products had similar, but slightly different NMR spectra: ($CDCl_3$) δ 1.2 (m, 6 H), 4.2 (m, 1 H). Upon treatment with aqueous 1 M NaOH for 0.5 h at 25 °C each was converted to the same 20:1 mixture of isomers (GLC analysis). The lesser product was therefore assigned the cis structure.

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Registry No.—*cis*-2-Methylnitrocyclopropane, 66303-44-4; *trans*-2-methylnitrocyclopropane, 15267-24-0; 1,3-dibromobutane, 107-80-2.

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Kinetic and Equilibrium Acidities of 3-Nitropropene and Some of Its Derivatives

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Rates of hydroxide ion deprotonation in water for 3-nitropropene and seven of its derivatives, $R_2R_3C{=}C(G)$-$CH(R_1)NO_2$, where R_1, R_2, and R_3 are either H or Me, and G is H, Me, Ph, or Br, have been measured and compared with their equilibrium acidities in water. These substitutions were found to cause a complex variation of kinetic and equilibrium acidities which was interpreted by assuming that the kinetic acidities were governed primarily by polar effects and steric inhibition of solvation in the transition state, whereas the equilibrium acidities were governed primarily by steric strains in the product nitronate ions. It was concluded that nitroalkane (and other carbon acids) deprotonations usually fail to conform to the Leffler–Grunwald rate–equilibrium relationship when the structural changes are made in the carbon acid. The rates of deprotonation in water for 3-nitropropene, 3-nitropropene-3,3-d_2, and 1-nitro-2-butene by pyridine and seven methyl-substituted pyridines were determined. The k_H/k_D isotope ratios were found to vary from 8.5 to 11.4. A Brønsted β of 0.59 was obtained. The significance of these data with respect to the mechanism of deprotonation of nitroalkanes is discussed.

In earlier papers in this series we have examined rates of deprotonation, equilibrium acidities, and isotope effects for a variety of nitroalkanes in an attempt to elucidate the mechanisms of deprotonation of carbon acids by bases.[2] It appeared to be of interest to extend the study of 3-nitropropene and some of its derivatives, since it was anticipated that these β,γ-unsaturated nitroalkanes, which are much more acidic than their saturated analogues, would provide useful information with regard to rate–equilibrium relationships and the variation in the size of k_H/k_D isotope effects with the strength of the base used in the deprotonation.

Results

Rates of proton removal from the β,γ-unsaturated nitroalkanes by hydroxide ion were measured spectrophotometrically in water at 25 °C under pseudo-first-order conditions. The kinetics were followed by stopped-flow except for 2-methyl-3-nitro-1-butene and 2-nitro-3-pentene, where the rates were measured on a Beckman Kintrac VII spectrophotometer. For 3-nitropropene, 1-nitro-2-butene, and 3-methyl-1-nitro-2-butene pK's were measured potentiometrically by a partial neutralization technique; other pK's were

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