to *trans*. For the 3-*t*-butylthietane 1-oxides, **2a** and **2b**, isomer purity could be quantitatively determined from vapor phase chromatography.[16] For the 3-*p*-chlorophenylthietane 1-oxides, **1a** and **1b**, a qualitative analysis of isomer purity was allowed from the nmr spectra, but quantitative determinations could only be made by integration of the nmr signal for the β-hydrogens in the α-tetradeuterated sulfoxides.

Stereomutation of sulfoxides[17] may be effected either by heat or light, or by the action of reagents such as hydrogen chloride or dinitrogen tetroxide. Both chemical and thermal equilibration of the 3-substituted thietane 1-oxides yielded mixtures of similar isomer ratios (Table I).

Thermally induced racemization of mixtures of differing isomer ratios of **2a** and **2b** in purified decalin under nitrogen at 170–175° led to establishment of equilibrium in less than 15 min; despite the difference in temperature, the position of equilibrium was nearly the same as in the catalyzed equilibrations (Table I).

The sulfone **1c** on treatment with sodium deuterioxide in a deuterium oxide–dioxane solution was converted to the tetradeuterated sulfone.[18] Reduction of the sulfone with lithium aluminum hydride in ether yielded the tetradeuterated sulfide **1**-d_4 and oxidation of the sulfide with sodium metaperiodate yielded a mixture of the two α-deuterated sulfoxides, **1a**-d_4 and **1b**-d_4. Equilibration of this mixture with hydrochloric acid in dioxane yielded an isomer ratio in fair agreement with ratios obtained from the *t*-butyl system (Table I).

Recent calculations[19] have substantiated the earlier suggestion[3] that the axial preference exhibited by sulfinyl oxygen in thiane 1-oxides may result from an attractive van der Waals interaction between the oxygen and carbons 3 and 5 or their attached axial hydrogens. No repulsive interactions were calculated between the oxygen and carbons 3, 4, or 5 or any of their attached hydrogens.

Usually the preferred geometry for 1,3 disubstitution on a nonplanar cyclobutane ring is *cis* diequatorial, attributed to the tendency to minimize 1,3 (cross-ring) nonbonded repulsions.[20,21] In the puckered thietane ring where a bulky substituent at C_3 exerts an equatorial preference, the oxygen is forced to assume a pseudoaxial or pseudoequatorial position. The experimental observation that 3-substituted thietane 1-oxides prefer the *cis* (diequatorial) geometry would appear to be the result of a repulsive interaction between oxygen and carbon 3 and/or its attached axial hydrogen in the *trans* isomer; depending on the degree of puckering the nonbonded distances of concern may be significantly shorter than in the thiane 1-oxide case.

---

[16] A 5-ft FFAP column was employed.

[17] K. Mislow, *Record Chem. Progr.*, **28**, 217 (1967).

[18] J. Weinstock, J. L. Bernardi, and R. G. Pearson, *J. Am. Chem. Soc.*, **80**, 4961 (1958).

[19] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, **91**, 337 (1969).

[20] J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3884 (1965).

[21] K. B. Wiberg and G. M. Lampman, *ibid.*, **88**, 4429 (1966).

[22] (a) Alfred P. Sloan Research Fellow, 1965–1968; (b) National Aeronautics and Space Administration Trainee, 1967–1969.

Carl R. Johnson,[22a] **Walter O. Siegl**[22b]
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received January 27, 1969

The Effects of Structure on the Rates of Neutralization and the Ionization Constants of Nitrocycloalkanes

Sir:

Previous studies of the effects of structure on the rates of neutralization and the ionization constants of nitro compounds reveal that nitroalkanes which neutralize relatively rapidly may be much weaker than more slowly neutralized but yet stronger homologs. The reactivities for neutralization of the indicated nitroalkanes by aqueous hydroxide ion (k_2, M^{-1} min^{-1}, 0°) are: nitromethane (238) > nitroethane (39.1) > 2-nitropropane (2.08); that for dissociation ($K_{\text{ion}} \times 10^{11}$, 25°), however, is 2-nitropropane (1980) > nitroethane (252) > nitromethane (5.75).[1] The nucleophilicities for reversal in these systems are thus $CH_2NO_2^- > CH_3CHNO_2^- > (CH_3)_2CNO_2^-$. The striking behavior of these ions has been attributed to dielectric[1b] and electronic and steric effects[2] and to reduction of the nucleophilicities of electron-rich nitronates resulting from hydrogen-bonded solvation at nitronate oxygens.[2]

A study has now been made of the effects of ring size on the rates of neutralization and the ionization constants of homologous nitrocycloalkanes. The objectives of this investigation are to evaluate structural influences on the kinetics and thermodynamics of formation of cycloalkanenitronates.

Neutralizations of nitrocycloalkanes were studied as second- and as first-order processes using rapid conductometric methods in which consumption of the bases was essentially complete, oxidants were excluded, and the nitro compounds could be regenerated almost quantitatively. The kinetic data were satisfactorily accurate and the results are summarized in Table I.

The conductometric reactivities for neutralization of nitrocycloalkanes are: $4 > 5 > 7 > 8 > 6 \gg 3$. The results of interest are: (1) nitrocyclobutane neutralizes faster than any of its higher homologs, (2) nitrocyclopropane does not undergo conductivity change, (3) the reactivity order of the C_4–C_8 nitrocycloalkanes is not altered by bases of different strengths,[3] and (4) except for nitrocyclopropane, nitrocycloalkanes neutralize more rapidly than their acyclic analogs.

Rapid neutralization of nitrocyclobutane is not predicted by I strain.[4] The kinetic results for neutralization of 1-deuterionitrocyclobutane, 1-deuterionitrocyclopentane, and 1-deuterionitrocyclohexane by hydroxide (Table I) do not reveal any difference in reaction mechanism of these homologs. The near-maximum isotope effects observed, $k_H/k_D \cong 8.3$–8.9 at 0°, indicate that in neutralization of nitrocycloalkanes the reacting carbon–hydrogen bond is highly broken and that between hydroxide and the removable proton is weakly developed (I). The remarkable behavior of nitrocyclobutane may be due, in combination, to the s character of the electrons of the removable hydrogen and to the favorable geometry for attack on hydrogen which will allow (partial) delocalization involving the

---

[1] (a) D. Turnbull and S. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943); (b) G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

[2] M. Fukuyama, P. W. K. Flanagan, and H. Shechter, submitted for publication, and references therein.

[3] The reactivities of the nitrocycloalkanes do reflect the strengths of the neutralizing bases. The strengths of the indicated bases in isopropyl alcohol are: ethoxide > hydroxide > methoxide > glycoloxide. J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

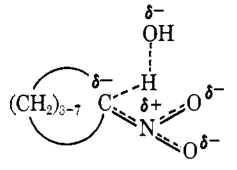
[4] H. C. Brown and M. Bordowski, *ibid.*, **74**, 1884 (1952).

Table I. Rates of Neutralization and Ionization Constants of Nitro Compounds

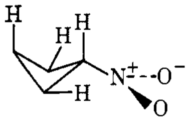
	OH⁻,[a] dioxane–H_2O[e]			OH^-,[b] glyme–H_2O[e]	CH_3O^-,[b] CH_3OH	$C_2H_5O^-$,[b] C_2H_5OH	$HOCH_2CH_2O^-$,[b] $HOCH_2CH_2OH$	$K_{ion} \times 10^{10}$ [c] 33% (w/w) CH_3OH–H_2O	Reversal[d] $(CH_2)_{3-7}C{=}NO_2^-$
Compound	k_2[f]	$\Delta H^{\ddagger}$[g]	$\Delta S^{\ddagger}$[h]	k_2[f]	k_2[f]	k_2[f]	k_2[f]	k_2[f]	Rel rates
Nitrocyclopropane	*i*			*i*		*i*		*i*	
Nitrocyclobutane	165	12.5	−10.6	143	26.0	291	18.8	2.96	1930
Nitrocyclopentane	39.8	11.7	−16.4	41.9	7.67	132	7.63	122	113
Nitrocyclohexane	7.60	13.1	−14.5	8.11	2.13	24.5	1.39	12.1	21.8
Nitrocycloheptane	20.6	12.1	−16.2	24.2	5.51	79.2	5.42	225	3.17
Nitrocyclooctane	16.0	11.7	−18.1	18.8	4.40	58.2	2.79	554	1
Nitrocyclobutane-1-*d*	19.5	13.3	−11.9						
Nitrocyclopentane-1-*d*	4.80	12.8	−16.5						
Nitrocyclohexane-1-*d*	0.86	14.6	−13.3						
2-Nitropropane	8.03			11.0	1.46	32.9	2.37		
3-Nitropentane	1.69								
4-Nitroheptane	0.71								

[a] Determined using the methods of S. H. Maron and V. K. La Mer, *J. Am. Chem. Soc.*, **60**, 2588 (1938). [b] Determined as pseudo-first-order processes using excess nitro compound. [c] Determined by the method of ref 1a. [d] Calculated as $k_{-2}'/k_{-2} = K_{HA}k_2'/K_{HA}'k_2$ for $HA + OH^- \rightleftarrows A^- + H_2O$. Using k_2 obtained in 50% dioxane–water at 0° and K_{ion} in CH_3OH–H_2O does not lead to serious errors in the relative rates. [e] 50% (v/v). [f] $M^{-1}\ min^{-1}$, 0°. [g] kcal/mole. [h] cal/deg mol. [i] Immeasurably small.

nitro group and advantageous solvation of the carbanionic transition state derived from the relatively rigid nitrocycloalkane (II). In the transition state from



I

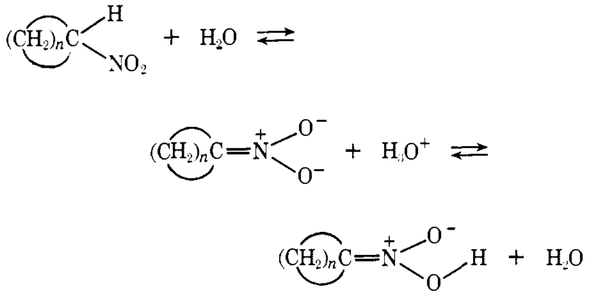


II

nitrocyclobutane, interactions of α,α′-hydrogens with the solvated oxygens of the nitro group are expected to be less than that for the C_5–C_6 homologs and thus the nitro group can assume more readily the preferred geometry (the plane of the nitro group is perpendicular to the bond to removable hydrogen) for delocalization. In the carbanionic transition state for nitrocyclobutane there may also be advantageous compromise between pyramidal stereochemistry and that allowing sp^2 hybridization through the nitro group. The greater reactivities of C_5, C_7, and C_8 than of C_6 nitrocycloalkanes are consistent with theory of steric effects in monocyclic systems in which a tetragonal ring atom acquires trigonal character during reaction.[4] In part, however, as for nitrocyclobutane, the reactivity of nitrocyclopentane may be derived from exposure of its removable proton, favorable conformation of its nitro group, and enhanced solvation of its transition state.

Although nitrocyclopropane does not respond conductometrically, the cyclopropanenitronate anion could be formed rapidly. Much more rapid reversal to nitrocyclopropane might occur resulting in equilibria undetected by the conductometric method. Deuterium exchange into *trans*-2-ethylnitrocyclopropane (1.65 *M*) by D_2O (9.7 *M*)-triethylamine (0.21 *M*) in dimethylformamide, however, does not occur detectably in 350 hr (25°). Under similar conditions 2-nitropropane (3.1 *M*) is 90% exchanged in 40 min. The resistance of nitrocyclopropanes to bases must be related primarily to restrictions in exocyclic delocalization in transition states leading to cyclopropanenitronates. Neutralization of a nitrocyclopropane is also expected to be retarded on the basis of the large angle between its removable hydrogen and its nitro group and if its cyclopropyl and nitro groups occupy a restricted *cis*-bisected conformation.

The apparent ionization constants of nitrocycloalkanes (eq 1) as a function of ring size, as determined potentiometrically (Table I), are 8 > 7 > 5 > 6 > 4 ≫ 3. The order implies that steric factors are important.[4]



(1)

The rates of neutralization of the nitrocycloalkanes, except for nitrocyclopropane, do not correlate, however, with their dissociation constants, and the kinetic reactivities (Table I) for hydrolysis of cycloalkanenitronates to nitrocycloalkanes are $C_4 > C_5 > C_6 > C_7 > C_8$. Nitrocyclobutane neutralizes and cyclobutanenitronate reverses more rapidly than do their higher homologs; thus nitrocyclobutane is weaker than its C_5–C_8 homologs because of the much greater rate of proton transfer to cyclobutanenitronate. The marked reactivity of cyclobutanenitronate is derived from its internal strain and, from principles of microscopic reversibility, from the advantageous transition state for proton transfer. The hydrolytic reactivities of the C_5–C_6 cycloalkanenitronates are not predicted by steric effects involving coordination number change.[4] The relatively rapid reversal of cyclopentanenitronate may arise from the relatively limited steric resistance to proton transfer in its solvated transition state.

Acknowledgment. This research was sponsored in part by the Office of Ordnance Research, the Research Corporation, and the National Science Foundation.

P. W. K. Flanagan, H. W. Amburn
H. W. Stone, J. G. Traynham, H. Shechter
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received February 25, 1969