Stable Carbonium Ions. LXX.[1] Protonated Nitroalkanes and Nitroaromatic Compounds. Cleavage of Protonated Nitroalkanes (Cycloalkanes) to Carbonium Ions

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Abstract: Nitromethane, nitroethane, 2-nitropropane, 2-fluoro-2-nitropropane, and 1-nitro-2-methylpropane as well as various substituted nitrobenzenes were fully protonated in the strong acid system FSO_3H–SbF_5. The cleavage of nitroalkanes to the corresponding carbonium ions was also observed. The rate of rotation of the protonated nitro group in nitroaromatic compounds was studied by pmr spectroscopy. The rate of rotation in 3,5-dichloro-4-methylnitrobenzene at $-50°$ is $k = 100\ \text{sec}^{-1}$, and the activation energy is $\Delta H^{\ddagger} = 7$ kcal mol.

Nitro compounds are weak bases in sulfuric acid solution. Nitrobenzene is about 40% ionized in 100% sulfuric acid.[3] The reported value[4] of -11.9 for nitromethane in sulfuric acid indicates that nitromethane should be nearly completely protonated in FSO_3H ($H_0 = -13.8$). Deno, *et al.*,[5] studied the protonation of nitro compounds in sulfuric acid and oleum by pmr spectroscopy, but due to incomplete protonation and exchange under the experimental conditions used, the reported spectral values are of limited value. After the completion of our work, an nmr and ir spectroscopic study of protonated nitroalkanes in the strong acid systems HF–BF_3 and HF–SbF_5 was reported by Hogeveen.[6] As our own studies (in FSO_3H–SbF_5–SO_2 solution) overlapped only slightly with Hogeveen's work and contain significant new findings, we report them in full.

Table I. Pmr Spectra[a,b] of Nitroalkanes in FSO_3H–SbF_5–SO_2 Solution at $-60°$

	RNO_2 in SO_2			RNO_2 in FSO_3H–SbF_5–SO_2 at $-60°$			
	CH_3	CH_2	CH	CH_3	CH_2	CH	NO_2H^+
CH_3NO_2	4.30 (s) (neat liq)			5.42 (s)			17.1 (s)
$CH_3CH_2NO_2$	1.19 (t)	4.20 (q)		1.83 (t) $J = 6.7$	5.54 (q) $J = 6.7$		16.60 (s)
$(CH_3)_2CHNO_2$	1.52 (d) (neat liq)		4.68 (sp) $J = 6.5$	2.03 (d) $J = 6.5$		5.88 (sp) $J = 6.5$	16.60 (s)
$(CH_3)_2CFNO_2$	1.90 (d) (neat liq) $J = 19.5$			3.27 (s, br)			14.35
$(CH_3)_2CHCH_2NO_2$	1.02 (d) $J = 6.5$	3.22 (d) $J = 7.0$	1.95 (m)	1.22 (d) $J = 6.5$	5.20 (d) $J = 7.0$	[4.10 (m)] overlapped by $(CH_3)_3C^+$ion	16.58
$(CH_3)_3CNO_2$					$\sim 4 \times 10^6$ $(CH_3)_3C^+$		
c-$C_6H_{11}NO_2$		α 2.10 (m, br) β,γ 1.60 (m, br)	4.25 (m, br)	3.90 (m)	α 2.50 (m) β 4.12 (m)	Cyclopentylcarbinyl	

[a] δ (parts per million) from external TMS. J values are in hertz. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, sp = septuplet.

In continuation of our investigation of the protonation of weak organic bases in super acids we have now studied the behavior of nitroalkanes and nitroaromatic compounds in the strong acid system FSO_3H–SbF_5–SO_2, with particular emphasis on the structure of the protonated species and the question of the rotational barrier of the protonated nitro group.

Results and Discussion

Protonated nitroalkanes and protonated nitroaromatic compounds were obtained by protonation of the corresponding nitro compounds in FSO_3H–SbF_5–SO_2 solution generally at $-60°$. Pmr spectra of the ions were obtained and the data are summarized in Tables I and II. Using neat FSO_3H as solvent, the $-NO_2H^+$ peak could not be observed even at $-90°$, indicating fast exchange in this weaker acid system.

At $-60°$ nitromethane shows two sharp singlets at δ 5.42 and 17.1 (relative to capillary TMS). The peaks correspond to the methyl and $-NO_2H^+$ protons. In protonated nitroethane, the methyl absorption is a triplet ($J = 6.7$ Hz) at δ 1.83, the methylene absorptions a quadruplet ($J = 6.7$ Hz) at δ 5.54, and the $-NO_2H^+$ proton is at δ 16.60. Protonated 2-nitropropane shows a doublet for the methyl at δ 2.03 and a septuplet for the α proton at 5.88 while the NO_2H^+

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(1) Part LXIX: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **90**, 6087 (1968).

(2) Postdoctoral Research Investigator, 1967–1968.

(3) R. J. Gillespie, *J. Chem. Soc.*, 2542 (1950).

(4) R. J. Gillespie and C. Solomons, *ibid.*, 1796 (1957).

(5) N. C. Deno, R. W. Gaugler, M. J. Wisotsky, *J. Org. Chem.*, **31**, 1968 (1966).

(6) H. Hogeveen, *Rec. Trav. Chim. Pays Bas*, **89**, 1320 (1968).

Table II. Pmr Spectra[a],[b] of Nitroaromatic Compounds in $FSO_3H-SbF_5-SO_2$ Solution at −60°

	Compound			Ion				
	CH_3	CH	Temp, °C	CH_3	*o*-CH	*m*-CH	*p*-CH	NO_2H^+
$C_6H_5NO_2$		*ortho* 7.80 (m)	0		8.76	7.99	8.46	
		meta 7.30 (m)	−100		8.55	7.95	8.41	15.53
		para			9.04			
p-$ClC_6H_4NO_2$		6.34 (d)	−60		8.90 (s, br)	8.17 (d)		
		6.98 (d)	−90		8.67 (d)			
					9.13 (d)	8.17 (d)		16.00
p-$FC_6H_4NO_2$		*ortho* 8.12 (m)	−20		9.02 (br)	7.83 (m)		
		meta 7.13 (m)	−80		9.36 (br)			
					8.82 (br)			15.61
p-$CH_3C_6H_4NO_2$	2.11 (s)	7.07 (d)	−25		8.71 (s, br)	7.90 (d)		
		7.77 (d)	−70		8.56 (d)	7.92 (d)		
		J = 9.0			9.01 (d)			15.02
					J = 9.0			
4-CH_3-3,5-$Cl_2C_6H_2NO_2$	2.50 (s)	8.17 (s)	−40	2.88 (s)	8.82 (s)			
			−100		8.62 (d)			
					9.13 (d)			
					J = 2.2			16.20
2,4,6-$(CH_3)_2C_6H_2NO_2$	2.13 (s)	6.95 (s)		2.60 (s)	7.55 (s)			14.50
	2.22 (s)			2.85 (s)				
2,5-$(CH_3)_2C_6H_3NO_2$	2.17	7.02 (m)		2.74 (s)	8.92 (s, br)	7.87 (d)	8.27 (d)	14.82
	2.30	7.46 (s)		2.97 (s)				

[a] δ (parts per million) from external TMS. J values are in hertz. [b] s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

proton appears as a singlet at δ 16.60. In no case can coupling between the CH and NO_2H^+ protons be observed.

In the hope of observing coupling between the NO_2H^+ proton and the α-fluorine, 2-fluoro-2-nitropropane was studied in the acid system. No coupling of the fluorine to the NO_2H^+ proton was observed and even the fluorine coupling to the methyl groups was no longer present. The methyl signal, which appears as a sharp doublet at δ 1.90 (J = 19.5 Hz) in the starting material, appears as a broad singlet at 3.27 in $FSO_3H-SbF_5-SO_2$. The loss of coupling is attributable to rapid exchange of the fluorine atom with the acid system such as is observed with methyl fluoride in SbF_5-SO_2 solution.[7] During preparation of the sample at −80°, a considerable amount of fluorodimethylcarbonium ion[8] is also formed as evidenced by the pmr doublet at δ 4.05 shown in Figure 1. Confirmatory evidence for the $CH_3{}^+CFCH_3$ ion was obtained from the ^{19}F resonance spectrum showing a septuplet at ϕ −182. Attempts to observe protonated 2-nitro-2-fluoropropane in neat FSO_3H where fluorine exchange was expected to be of lesser importance failed even at −85° because of rapid exchange of the proton on oxygen in this weaker acid system. NO^+ was identified by ir and Raman spectroscopy.

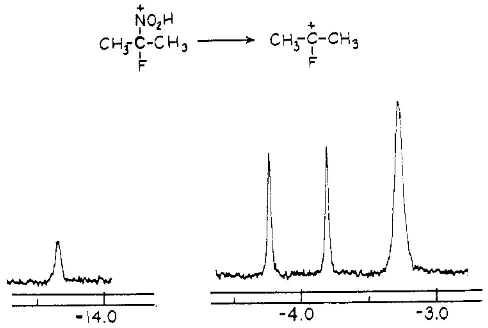
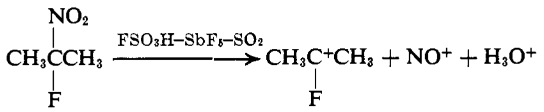
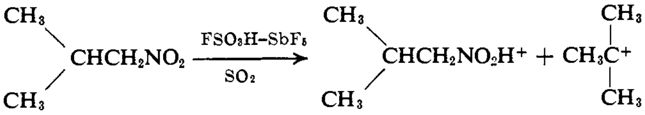


Figure 1. Pmr spectrum (60 MHz) of 2-fluoro-2-nitropropane in $FSO_3H-SbF_5-SO_2$ at −60°. The broad singlet at δ 3.27 is due to the methyl groups of the protonated species. The sharp doublet at δ 4.05 is due to the fluorodimethylcarbonium ion.



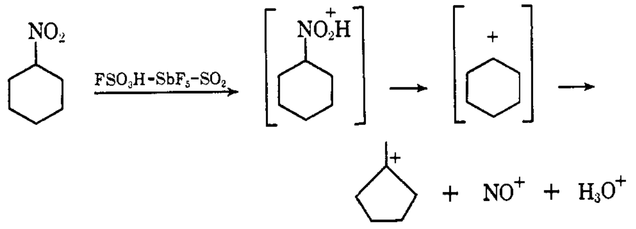
$$CH_3\overset{NO_2}{\underset{F}{C}}CH_3 \xrightarrow{FSO_3H-SbF_5-SO_2} CH_3\underset{F}{C^+}CH_3 + NO^+ + H_3O^+$$

When an SO_2 solution of 1-nitro-2-methylpropane is added to 1:1 FSO_3H-SbF_5 at −80°, the *t*-butyl cation is formed as well as the protonated nitro compound. At −20° protonated 1-nitro-2-methylpropane does not decompose to the *t*-butyl cation at an appreciable rate. The *t*-butyl cation formed thus may be due to local overheating during preparation of the sample.



$$(CH_3)_2CHCH_2NO_2 \xrightarrow[SO_2]{FSO_3H-SbF_5} (CH_3)_2CHCH_2NO_2H^+ + CH_3\overset{CH_3}{\underset{CH_3}{C^+}}$$

Nitrocyclohexane in $FSO_3H-SbF_5-SO_2$ at −80° cleaves cleanly to 1-methylcyclopentyl cation[9] leaving no protonated nitro compound. 2-Nitro-2-methylpropane in $HF-BF_3$ solution cleaves to the *t*-butyl cation and the protonated nitro compound cannot be observed.[9] Protonated nitro compounds thus can cleave to the corresponding carbonium ions, secondary and tertiary ones cleaving much more easily than primary nitro compounds.



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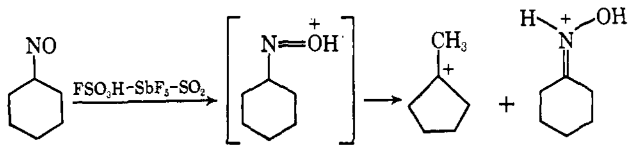
[7] G. A. Olah and M. B. Comisarow, unpublished results.

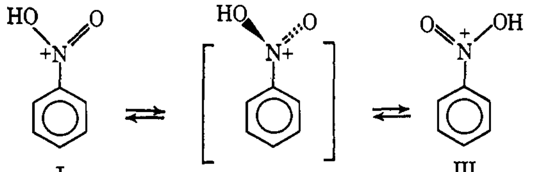
[8] G. A. Olah, R. Chambers, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **89**, 1268 (1967).

[9] G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *ibid.*, **89**, 2692 (1967).

When nitrosocyclohexane in SO_2 solution was added to FSO_3H–SbF_5, a white precipitate formed which dissolved upon warming and did not precipitate again upon cooling. The pmr spectrum of the clear solution showed the characteristic spectrum of 1-methylcyclopentyl cation and in addition protonated cyclohexanone oxime.[10] Protonated cyclohexanone oxime showed a broad multiplet centered at δ 2.20 due to the ring protons and two low-field peaks due to the NH proton and OH protons. The NH peak is at δ 12.40 (s, sharp) and the OH peak is at 11.43 (s, br). The 100-MHz pmr spectrum of protonated nitrobenzene at 0° shows good resolution of the ring protons, the *o*-, *m*-, and *p*-proton peaks being completely separated. The *o*-protons are at lowest field and the *m*-protons at highest field. A calculated spectrum[11] with the following chemical shifts and coupling constants showed good correlation with the experimental spectrum shown in Figure 2: $\delta H_1 = \delta H_5 = 8.76$; $\delta H_2 = \delta H_4 = 7.99$; $\delta H_3 = 8.46$; $J_{12} = J_{45} = 8.00$; $J_{13} = J_{35} = 1.00$; $J_{14} = J_{25} = 0.50$; $J_{15} = J_{24} = 1.00$; $J_{23} = J_{34} = 7.50$.



At temperatures below −20° the *o*-proton peak of protonated nitrobenzene is broadened. The temperature at which maximum broadening occurs, T_c, is −65°. Below −65°, the *o*-proton peak begins to sharpen and at −80° the original doublet has become two doublets separated by 29 Hz (at 60 MHz). The upfield doublet overlaps the *p*-proton peak. We attribute this temperature dependence to the hindered rotation of the protonated nitro group. When rotation is fast the *o*-protons are equivalent and the higher temperature spectrum (>−20°) is observed. When the rotation is slowed sufficiently (−80°) the *o*-protons have different chemical shifts. The temperature dependence of the spectrum could also be accounted for by intramolecular proton exchange through a symmetrical transition state, IV.



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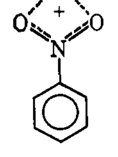

IV

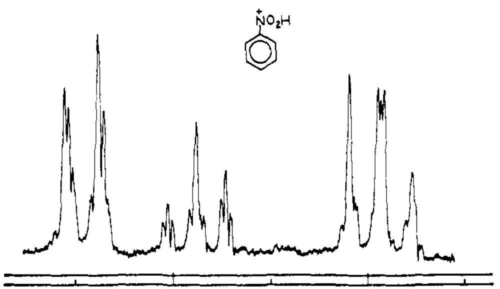

Figure 2. Pmr spectrum (100 MHz) of protonated nitrobenzene at 0°. The *o*-protons are at lowest field and the *m*-protons at highest field.

That the temperature dependence is indeed due to hindered rotation of the protonated nitro group can be inferred from the effects of ring substituents. The coalescence temperature for protonated 4-nitrotoluene is 27° higher than that for nitrobenzene, occurring at −38°. A *p*-methyl substituent would be expected to affect rotation but not intramolecular proton exchange. No temperature dependence of protonated nitromesitylene is observed. Two *o*-methyl groups might be expected to raise the energy of the conformations with the nitro group in the plane of the ring (I and III) relative to the transition state for rotation with the plane of the nitro group perpendicular to the plane of the ring (II). The coalescence temperature might then be lowered below the accessible region. The spectrum of 2,4-dimethylnitrobenzene shows no temperature dependence, supposedly because one conformation is much more stable than the other. In Table III are shown coalescence temperatures for substituted protonated nitrobenzenes.

Table III. Coalescence Temperatures of the *o*-Protons for Rotation of the Protonated Nitro Group in Substituted Nitrobenzenes[a]

Compound	T_c, °C
Nitrobenzene	−65
4-Methylnitrobenzene	−38
4-Fluoronitrobenzene	−58
4-Chloronitrobenzene	−62

[a] The peak separation in the absence of rotation was about 29 Hz at 60 MHz in each case.

In order to determine the activation energy for rotation, the temperature dependence of the pmr spectrum of protonated 3,5-dichloro-4-methylnitrobenzene was studied. In Figure 3 are shown the experimental spectra at various temperatures and the computed spectra[12] at various exchange rates. Matching of the line shapes allows the activation energy to be determined as $\Delta H^{\ddagger} = 7$ kcal/mol.

Further indication of the polarizing ability of the protonated nitro group is provided by the fluorine shifts of *o*-, *m*-, and *p*-fluoronitrobenzenes. The shifts of the fluorine atoms, relative to those in the unprotonated nitro compounds for *ortho*, *meta*, and *para* positions, are ϕ 20.3, 4.84, and 37.1. Unlike protonated nitrobenzene in which the *o*-protons are at lowest field, the *p*-fluorine atom shows the greatest deshielding.

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(10) Protonated acetone oxime and acetophenone oxime were previously reported: G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4671 (1968).

(11) The LAOCOON III program of Professor A. A. Bothner-By, Carnegie-Mellon Institute, Pittsburgh, Pa., was used to calculate the theoretical spectrum.

(12) The calculation was a Gutowsky–Holm type carried out with a program written by Professor H. S. Gutowsky, University of Illinois, Urbana, Ill.

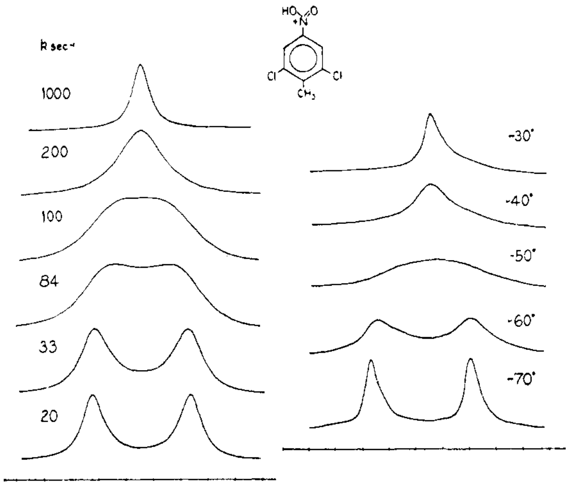

Figure 3. Temperature dependence of the ring proton peaks of protonated 3,5-dichloro-4-methylnitrobenzene. Experimental spectra at various temperatures are shown at the right and theoretical spectra at various rates of rotation of the NO_2^+H group at the left.

Protonation of aromatic dinitro compounds such as *m*-dinitrobenzene and 1,5-dinitronaphthalene showed that even the "magic acid" solvent system was not sufficiently strong to slow exchange rates enough to make observation of the NO_2H^+ protons possible. 4-Nitropyridine N-oxide is apparently diprotonated. The NOH^+ proton appears as a singlet at δ 11.0 while the ring pattern is an AB quartet very similar to that of the starting material centered at 9.32; the NO_2H^+ proton is, however, not observable due to exchange. If the compound were protonated only on the N-oxide oxygen the doublets of the AB quartet would be expected to be much more widely separated than those of the starting material.

Experimental Section

2-Nitro-2-fluoropropane[13] was prepared by reaction of perchloryl fluoride[14] with 2-nitropropane. 1-Nitro-2-methylpropane[15] was prepared from isobutyl bromide and sodium nitrite in DMSO. Nitromesitylene[16a] and 2,5-dimethylnitrobenzene[16b] were prepared by nitration of mesitylene and *p*-xylene. 3,5-Dichloro-4-methylnitrobenzene[17] was prepared by chlorination of 4-nitrotoluene. All other nitro compounds used were commercially available. Nitrosocyclohexane[18] was prepared from cyclohexylamine and peracetic acid.

Protonation of the nitro compounds was accomplished by dissolving 0.2 g of the nitro compounds in 2 ml of sulfur dioxide and adding 2 ml of cold 1:1 FSO_3H-SbF_5. Upon stirring, a clear solution was obtained.

Nmr spectra were obtained on a Varian Associates Model A56-60 spectrometer. The Univac 1107 computer of the university computing center was used for calculating theoretical spectra.

Acknowledgment. Support of this work by grants of the National Science Foundation and the U. S. Army Research Office, Durham, N. C., is gratefully acknowledged.

(13) H. Schecter and E. Johnson, *J. Org. Chem.*, **25**, 175 (1960).

(14) Perchloryl fluoride was obtained from the Pennsalt Chem. Co.

(15) N. Kornblum, *et al.*, *J. Amer. Chem. Soc.*, 78, 1497 (1956).

(16) A. V. Topchiev, "Nitration of Hydrocarbons," Pergamon Press, New York, N. Y., 1959: (a) p 32; (b) p 23.

(17) W. Davis, *J. Chem. Soc.*, 806 (1922).

(18) W. D. Emmons, *et al.*, *J. Amer. Chem. Soc.*, 79, 6522 (1957).

Stable Carbonium Ions. LXXI.[1] Protonated Imides

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Abstract: A series of imides have been studied in $FSO_3H-SbF_5-SO_2$ and/or $HF-SbF_5-SO_2$ solution. Succinimide, maleimide, N-methylmaleimide, 3,3-dimethylglutarimide, 3-ethyl-3-methylglutarimide, N-methyldiacetamide, and phthalimide were O-diprotonated as observed by low-temperature ^1H and ^{15}N nmr spectroscopy. Barbituric acid was triprotonated and pyromellitic diimide was O-tetraprotonated in the extremely strong acid system.

Imides are weak acids capable of forming salts with alkalis. The two acyl substituents more than compensate for the basicity inherent in the nitrogen atom. Phthalimide ($K_a = 5 \times 10^{-9}$) and succinimide ($K_a = 3 \times 10^{-11}$) are sufficiently acidic to dissolve in cold dilute aqueous sodium hydroxide solution.[3] Imides, however, unlike amines, do not have basic properties in water solution. The electron pair of nitrogen is partly delocalized over the carbonyl groups. The stabilization so gained would be lost if protonation would take place on nitrogen. Thus protonation of the carbonyl oxygen atoms is expected rather than addition of the proton onto nitrogen. No experimental study of the protonation of imides has so far been reported in the literature. In continuation of our studies of the protonation of weak organic bases, we now extended our investigations to protonated imides.

Results and Discussion

Although protonation of one of the carbonyl oxygen atoms of an imide (**1**) is expected to be more favorable than N-protonation (**2**), this suggestion had not been experimentally confirmed.

Protonation of the following imides was examined in $FSO_3H-SbF_5-SO_2$ and/or $HF-SbF_5-SO_2$ solution: succinimide, maleimide, N-methylmaleimide, 3,3-dimethyl-

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(1) Part LXX: G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 6461 (1968).

(2) Postdoctoral Research Investigator, 1967–1968.

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