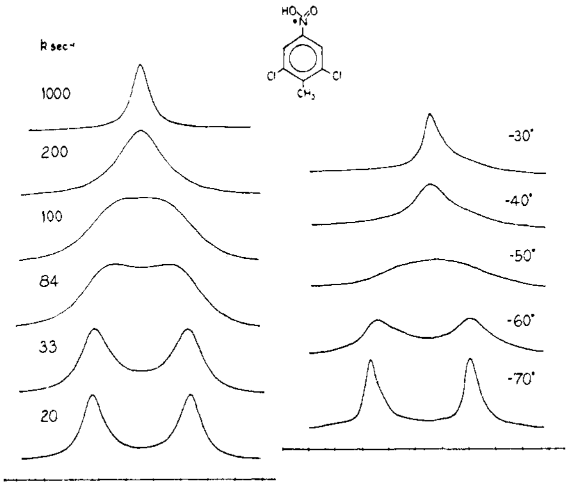

Figure 3. Temperature dependence of the ring proton peaks of protonated 3,5-dichloro-4-methylnitrobenzene. Experimental spectra at various temperatures are shown at the right and theoretical spectra at various rates of rotation of the NO_2^+H group at the left.

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

George A. Olah and Richard H. Schlosberg[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received May 2, 1968

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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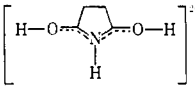
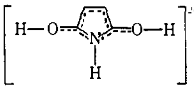
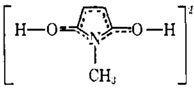
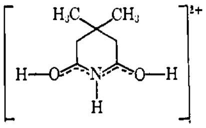
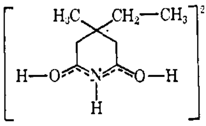
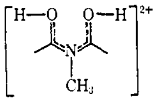
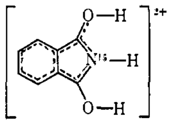
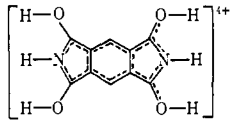
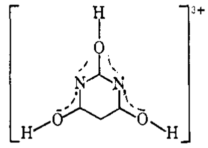
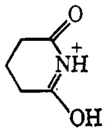
(1) Part LXX: G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 6461 (1968).
(2) Postdoctoral Research Investigator, 1967–1968.
(3) J. D. Roberts and M. J. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 553.

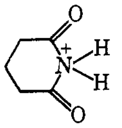
Table I. Pmr Chemical Shifts of Protonated Imides in $FSO_3H(HF)$-SbF_5-SO_2

Protonated imides	Temp, °C	δ, ppm[a]					
		CH₃	CH₂	CH	NH	N-CH₃	OH
	−80		4.35 (s)[b]		11.85 (s)		15.57 (s)
	−60			7.83 (s)	10.90 (s)		
	−80			7.80 (s)		3.72 (s)	12.80 (s)
	−80	1.23 (s)	3.50 (s)		11.87 (s)		15.07 (b)
	−40 −80	1.50 (s) 1.15 (t) J = 6.5	1.83 (q), J = 6.5 3.78 (s)		12.10 (s)		15.47 (s)
	−80 −20	3.58 (s) 2.92 (s) 3.17 (s)				4.13 (s) 3.85 (s) 3.88 (s)	15.56 (b)
	−80			8.43 (m)	10.87 (d) $J_{^{15}N-H}$ = 105		13.40 (s)
	−70			8.97 (s)	10.48 (s)		
	−80		6.97 (s)		12.42 (s)		11.77 (s)

[a] From external capillary of TMS. J values are in hertz. [b] Letters in parentheses represent multiplicity of peaks: s = singlet, b = broad singlet, m = complex multiplet, d = doublet, t = triplet, q = quartet.

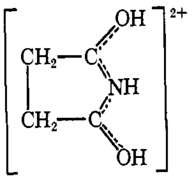
glutarimide, 3-ethyl-3-methylglutarimide, N-methyldiacetamide, phthalimide, barbituric acid, and pyromellitic diimide. The protonated species were observed by low-temperature nmr spectroscopy.


1


2

All imides studied were diprotonated in the super acid systems with both protons attached to the carbonyl oxygen atoms. Barbituric acid was triprotonated and pyromellitic diimide was multiprotonated in the super acids. The protonated imides give well-resolved pmr spectra. The N–H proton resonances are somewhat broadened due to the quadrupole interaction of the ^{14}N. At temperatures above −60° the broadening of the N–H resonance is substantially enhanced. In order to observe the protons on oxygen, it was necessary to record the spectra at temperatures of −60° or below. Above this temperature, exchange with solvent becomes faster than the nmr time scale and O–H proton resonances are washed out. Table I summarizes the pmr data of protonated imides.

A sulfur dioxide solution of **succinimide** when added to FSO_3H-SbF_5-SO_2 at −80° gives rise to an nmr spectrum (Figure 1) consisting of three singlets at δ 4.35, 11.85, and 15.57. The ratio of the peaks by integration of the spectrum is 4:1:2 representing the four C–H, one N–H, and two O–H protons, indicating the diprotonated imide **3**.


3

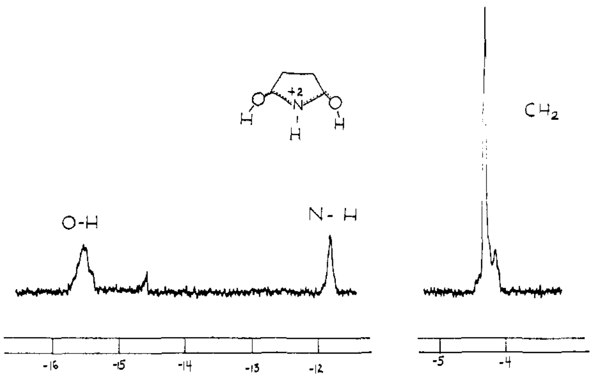


Figure 1.

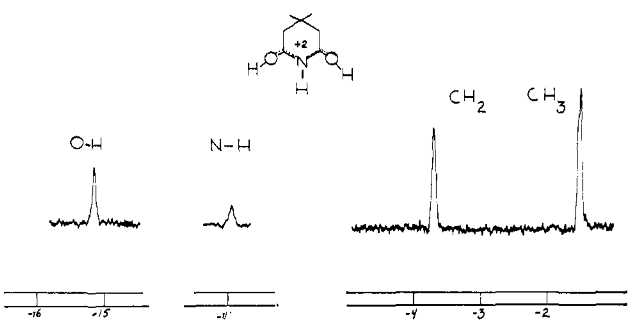
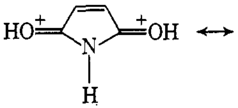
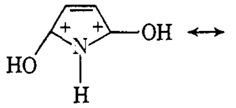
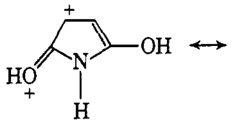


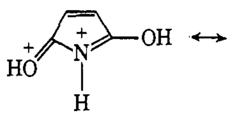
Figure 2.

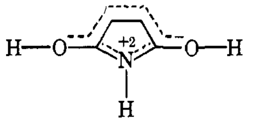
When a solution of **maleimide** in SO_2 is added to FSO_3H-SbF_5-SO_2 or HF-SbF_5-SO_2, the nmr spectrum shows only two peaks (disregarding the acid peaks). Even at −80° only singlets at δ 7.83 (two C-H protons) and 10.92 (one N-H proton) are observed. The OH protons are not observed, indicating rapid exchange even at this temperature. A comparison of the C-H chemical shift of **4** (7.83) with that of diprotonated N-methylmaleimide (7.80; *vide infra*) supports the conclusion that maleimide is diprotonated in strong acid. The structure of the rapidly exchanging diprotonated species may be formulated as in **4a-d** or **4e.**


4a


4b


4c


4d

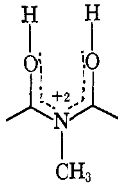

4e

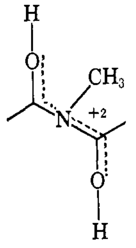
A clear greenish yellow solution was obtained when a solution of **N-methylmaleimide** in SO_2 was added to a solution of FSO_3H-SbF_5-SO_2 or (HF-SbF_5-SO_2) at −78°. The nmr spectrum of the species formed at −80° shows a sharp three-proton signal at δ 3.72 (N-CH_3), a sharp two proton resonance at 7.80 (vinyl H), and a broad singlet centered at 12.8 (O-H protons). No evidence for an N-H proton was observed.

3,3-Dimethylglutarimide in FSO_3H-SbF_5-SO_2 at −78° produced a clear, colorless solution. The nmr spectrum at −80° (Figure 2) showed sharp singlets at δ 1.23 (6 H, methyl protons), 3.50 (4 H, methylene protons), 11.87 (N-H proton), and 15.07 (2 H, O-H protons).

3-Ethyl-3-methylglutarimide in SO_2 added to a solution of FSO_3H-SbF_5-SO_2 at −78° gave rise to a clear, colorless solution. The nmr spectrum at −40° consisted of a triplet (J = 6.5 Hz) at δ 1.15 (3 H, methyl of ethyl group), a sharp singlet at 1.50 (3 H, C_3-methyl), a quartet (J = 6.5 Hz) at 1.83 (2 H, methylene protons of ethyl group), a sharp four-proton singlet at 3.78 (ring methylene protons), and a broad singlet at 12.10 (N-H). At −80° a sharp two-proton resonance is observed for the O-H protons at 15.47.

The nmr spectrum of the species formed from **N-methyldiacetamide** and super acid at −20° consists of two sharp singlets at δ 3.17 and 3.88 in the area ratio 2:1 (two acetyl methyls and one N-methyl). At −80° restricted rotation about the partially multiple C-N bonds leads to the observation of two pairs of singlets (two isomers). The O-H protons are seen at δ 15.56 (Figure 3).


5a


5b

Phthalimide is smoothly O-diprotonated in FSO_3H-SbF_5-SO_2 or HF-SbF_5-SO_2 solution at −78° to produce a clear yellow solution. Extensive delocalization of the positive charges into the aromatic nucleus is demonstrated by a comparison of the chemical shifts of the O-H protons in diprotonated phthalimide (δ 13.40) *vs.* those in diprotonated succinimide (15.6). The fact that the O-H protons are shielded by more than 2 ppm in diprotonated phthalimide indicates the greatly diminished electron deficiency on the carbonyl oxygens in the diprotonated species derived from the aromatic imide.

When potassium phthalimide with 95% ^{15}N was treated with HF-SbF_5-SO_2 at −78° it gave a clear yellow solution of the diprotonated labeled imide. The ^{15}N-H proton (Figure 4) appeared as a doublet ($J_{^{15}N-H}$ = 105 Hz) at δ 10.85. The coupling constant has been equated with the per cent s character of the N-H bond by the equation per cent s character = $0.43J_{^{15}N-H} - 6.0$.[4] This equation gives a value of 39% s character for diprotonated phthalimide and is consistent with a structure for the diprotonated species such as **6**.

The ^{15}N spectrum of diprotonated phthalimide shows a doublet centered at −125.6 ppm (relative to $^{15}NH_4^+$), about 10 ppm at lower field than the shift found for

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(4) G. Binsch, J. B. Lambert, B. W. Lambert, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5566 (1964).

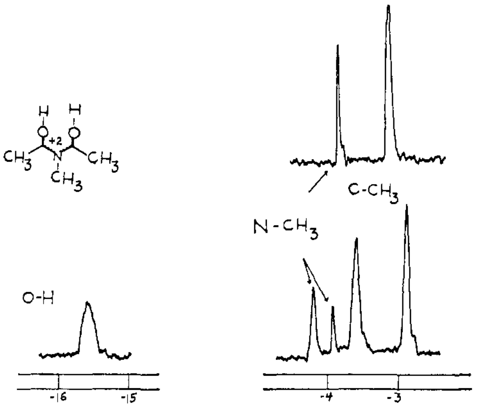


Figure 3.

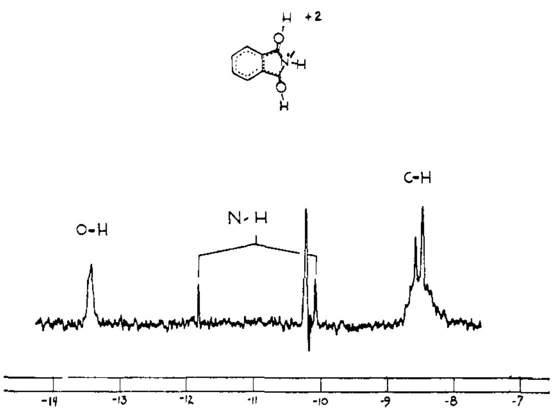
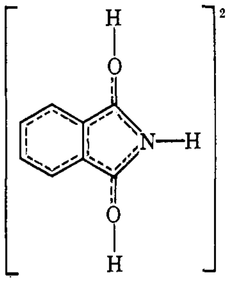
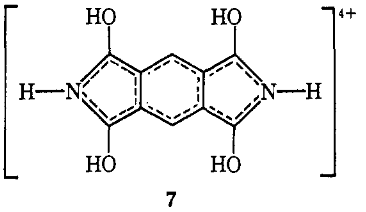


Figure 4.

$CH_3C\equiv{}^{15}N^+H$.[5] The shift was obtained with 95% ^{15}N-enriched potassium phthalimide by the indor method.[5] The ^{15}N chemical shift is dependent upon both the hybridization and the charge of the nitrogen atom. The greater amount of s character in protonated acetonitrile ($J_{^{15}N-H}$ = 136 Hz, 52% s character)[1] than in protonated phthalimide (39% s character) would indicate that the former compound should be more deshielded than the protonated imide. This, however, is more than compensated for by the greater charge delocalization in the case of the protonated imide than in the protonated nitrile. Thus there is less positive charge residing on the nitrogen of diprotonated phthalimide than on the nitrogen of protonated acetonitrile. If the correlation of ^{15}N chemical shift with charge on nitrogen for the series $CH_3C\equiv{}^{15}N^+H$ (−115 ppm relative to $^{15}NH_4^+$), $CH_3C\equiv{}^{15}N$ (−221 ppm), and $KC\equiv{}^{15}N$ (−255 ppm) is applicable, then the ^{15}N chemical shift for diprotonated phthalimide should be deshielded relative to the shift for $CH_3C\equiv{}^{15}N^+H$ where a much larger amount of positive charge resides on the nitrogen.



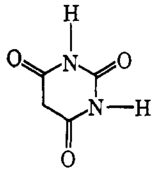
6



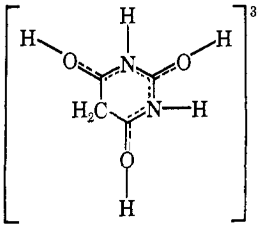
7

A suspension of **pyromellitic diimide** in SO_2 added to FSO_3H-SbF_5-SO_2 solution at −78° gave rise to a clear pale orange solution. The nmr spectrum consisted of a sharp singlet at δ 8.97 (2 H, aromatic protons) and a sharp singlet at 10.48 (2 H, N–H protons). Even at −94° exchange with the solvent was fast enough to preclude observation of any O–H resonance. The evidence is strong that pyromellitic diimide is symmetrically protonated, with **7** the probable tetraprotonated species.

Barbituric acid is shown to exist in the triketo form (**8**) by nmr spectroscopy. In DMSO-d_6 the spectrum consists of singlets at δ 3.40 (2 H, CH_2) and 11.10 (2 H, NH). The pmr spectrum of the protonated species in FSO_3H-Sb_5F-SO_2 at −80° consists of singlets at δ 6.97 (2 H, CH), 11.77 (3 H, O–H), and 12.42 (2 H, NH) which indicates the triprotonated species **9**.



8



9

Based on the prior observations that ureas[6] and β-diketones[7] are diprotonated in extremely strong acids, it is consistent therefore that imides are diprotonated as well.

Experimental Section

Imides used were commercial chemicals recrystallized prior to use. Potassium phthalimide-^{15}N was obtained from Merck Sharp and Dohme of Canada and was >95% ^{15}N. All nmr spectra were obtained on a Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe.

Generation of Diprotonated Imides in FSO_3H-SbF_5-SO_2 or HF-SbF_5-SO_2. In a typical experiment a solution or suspension (depending upon the solubility in SO_2) of the imide in SO_2 was slowly added to a tenfold (weight) excess of 1:1 $FSO_3H(HF)$-SbF_5 solution diluted with SO_2. After stirring for a short time (10–30 min) at −78° the solution became homogeneous.

Quenching of Protonated Species. The acid solution of the protonated imide in FSO_3H-SbF_5 or HF-SbF_5 was added dropwise to a slurry of methanol and sodium carbonate in SO_2 at −78°. After the solution was allowed to warm up to room temperature, the solvent was stripped off and the starting imide was isolated.

Acknowledgment. Support of the work through a grant of the National Institutes of Health is gratefully acknowledged.

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(5) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962); E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).

(6) G. A. Olah and A. M. White, *ibid.*, **90**, 6087 (1968).

(7) G. A. Olah and M. Calin, *ibid.*, 90, 4672 (1968).