

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 89, NUMBER 3

FEBRUARY 1, 1967

Physical and Inorganic Chemistry

Electron Spin Resonance Spectra of Free Radical Anions of Some Cyclic Anhydrides and Imides in Dimethylformamide Solution¹

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Abstract: Free radical anions of several cyclic imide and anhydride derivatives of phthalic and naphthalic acids have been generated electrolytically in dimethylformamide and their esr spectra have been measured. The Hückel and McLachlan molecular orbital calculations have been carried out for the compounds in question, and the calculated spin densities agreed well with values obtained from the experimental splitting constants. The C¹³ splittings in the spectra of the free radical anions of pyromellitic dianhydride and pyromellitic imide anhydride have been measured and analyzed using the method of Karplus and Fraenkel. A correlation was noted between the half-wave potentials of the first reduction waves of some of the compounds and the energies of the first antibonding molecular orbitals.

The investigation of free radical anions of various aromatic compounds by electron spin resonance has become a rather extensive field of chemical research providing information about the distribution of the unpaired spin density in the radicals which, in turn, depends on many factors, such as steric conditions in the radical, solvation, possibility of electron-exchange mechanisms, etc. The importance of the first of these factors in the free radical anions of aromatic carbonyl compounds has been pointed out in the papers of Stone and Maki³ and Rieger and Fraenkel.⁴

Carbonyl compounds are prone to undergo different rearrangements because of the possibility of keto-enol tautomerism; consequently, it might be expected that more than one free radical anion can be formed from the same initial compound depending on the conditions of the generation process.^{5,6}

(1) This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health. Part of the material has been presented at the 151th National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) On leave from Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland.

(3) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(4) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962).

It was of interest to us to extend such esr studies to various compounds possessing anhydride and imide linkages, and this paper is a brief report of our results obtained for free radical anions generated from solutions of phthalic and naphthalic imides and anhydrides. Some duplication of previous studies has been made since we were unaware of the unpublished work of Rieger.⁶

Experimental Section

The anion radicals in this work were prepared by electrolytic reduction in N,N-dimethylformamide using 0.03 M tetra-*n*-butylammonium iodide as the supporting electrolyte. The details of the apparatus and the procedure used for the generation of the free radicals have been described previously.^{7,8} The potentials at which the radicals were generated were determined from the half-wave potentials of the first reduction waves, which were measured on a Model PO4 polarizer.

Most of the chemicals were purchased from the City Chemical Co. and were used without further purification. The phthalimide that was used was recrystallized several times from ethanol.

(5) N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964).

(6) P. H. Rieger, Thesis, Columbia University, New York, N. Y., 1961.

(7) R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 5573 (1965).

(8) R. E. Sioda, D. O. Cowan, and W. S. Koski, *ibid.*, **89**, 230 (1967).

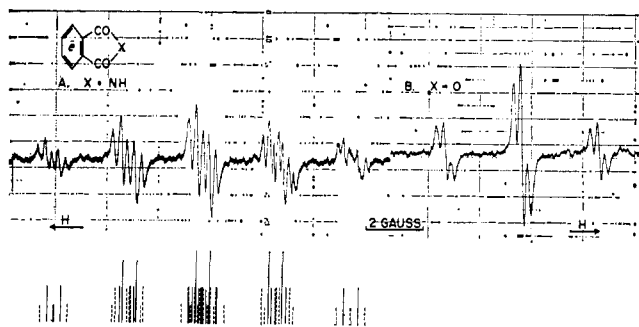


Figure 1. (A) Derivative esr spectrum of the free radical anion of phthalimide at -47.5° . The calculated line diagram constructed from splittings in Table I is given below. (B) Derivative esr spectrum of the free radical anion of phthalic anhydride at -43° .

Results

Phthalimide. When phthalimide was reduced at 22° , a very weak five-line spectrum was obtained. However, the intensity could be improved considerably by lowering the temperature of the solution (-10 to -50°). The spectrum obtained under such conditions has apparently 27 lines as is evident from Figure 1, and its g value is 2.0044. The spectrum could be interpreted in terms of splitting constants for two pairs of equivalent protons, one nitrogen atom, and another proton. Because of incomplete resolution, not all of the theoretically possible 54 lines were observed. The splitting constants are tabulated in Table I.

Phthalic Anhydride. This radical anion gives a reasonably intense spectrum at room temperature; however, lowering the temperature to -43° improves the resolution to such an extent that the broad triplet observed at room temperature is further split into three triplets. The splitting constants are tabulated in Table I, and a typical spectrum is given in Figure 1.

N-Phenylphthalimide. This compound on electrolysis gives a broad five-line spectrum at room temperature. At -42° a greater number of lines appears (Figure 2A), but they are considerably distorted, making the analysis uncertain. The spectrum is interpreted as resulting from splittings of a pair of equivalent protons, a nitrogen atom, and five nearly equivalent protons (Table I).

N-Phthalimidophthalimide. At room temperature an asymmetric esr spectrum, probably resulting from more than one species, is obtained. At -47° a spectrum of nine broad lines is obtained (Figure 4B) with evidence of additional small splittings. The main splitting is interpreted as resulting from a quartet of equivalent protons and a pair of nitrogens (Table I).

Pyromellitic Diimide. At room temperature this material gives, on reduction, an asymmetric esr spectrum apparently resulting from more than one free radical. At temperatures between -30 and -50° two different spectra can be observed depending on the value of the reduction potential. The first of these spectra (Figure 3B1) can be interpreted as arising from splittings from a pair of equivalent nitrogens and a pair of equivalent protons. The lines are relatively broad probably obscuring other details. This spectrum is due to the free radical anion of pyromellitic diimide. The other spectrum (Figure 3B2) appears to arise from the splitting of one nitrogen atom coupled to a pair of equivalent hydrogens. This spectrum corresponds to the free radical

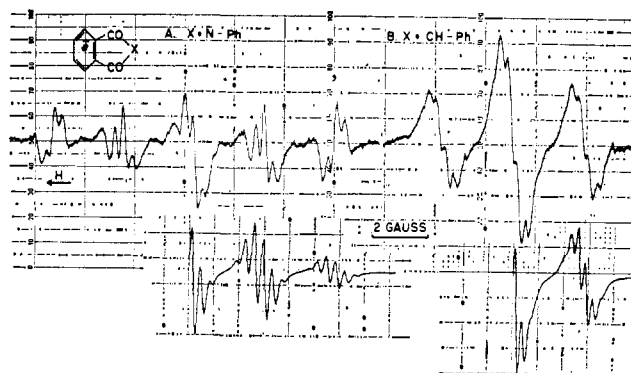


Figure 2. (A) Derivative esr spectrum of the free radical anion of N-phenylphthalimide at -42° . (B) Derivative esr spectrum of the free radical anion of 2-phenyl-1,3-indandione. The calculated spectra utilizing the SESRS computer program,³ Lorentzian line shape, and line width of 0.21 gauss is given below.

anion of the mixed imide anhydride of pyromellitic acid present as an impurity.^{6,9} On the sides of the latter spectrum, lines belonging to naturally abundant

Table I. Splitting Constants of the Radical Anions of Phthalic and Naphthalic Derivatives (in gauss)

Radical anion	Splitting const	Type of splitting ^a	Multiple
Phthalimide	2.65	1	2
	2.54	2	1
	0.46	1	1
	0.28	1	2
Phthalic anhydride	2.68	1	2
	0.27	1	2
N-Phenylphthalimide	2.58	1	2
	2.58	2	1
	0.32	1	5
2-Phenyl-1,3-indandione	2.58	1	2
	0.30	1	5
N-Phthalimidophthalimide	1.35	1	4
	1.35	2	2
	0.16	1	4
Triketohydrindene hydrate	1.07	1	4
	4.47	2	1
4-Nitrophthalimide	4.02	1	1
	2.95	1	1
	1.06	1	1
	8.75	2	1
3-Nitrophthalimide	3.60	1	1
	2.75	1	1
	0.88	1	1
Pyromellitic diimide	1.24	2	2
	0.72	1	2
Pyromellitic imide anhydride	0.99	2	1
	0.71	1	2
Pyromellitic dianhydride	0.71	1	2
	0.49	1	2
Secondary radicals (1)	0.18	1	1
	(2)	1.04	1
Naphthalimide	0.34	1	2
	4.17	1	2
	3.47	1	2
	0.57	1	2
	0.95	2	1
Naphthalic anhydride	0.38	1	1
	4.19	1	2
	3.62	1	2
	0.60	1	2

^a 1, splitting by proton; 2, splitting by nitrogen.

(9) The purchased pyromellitic diimide contains about 25% of the imide-anhydride of pyromellitic acid: private communication of City Chemical Corp.

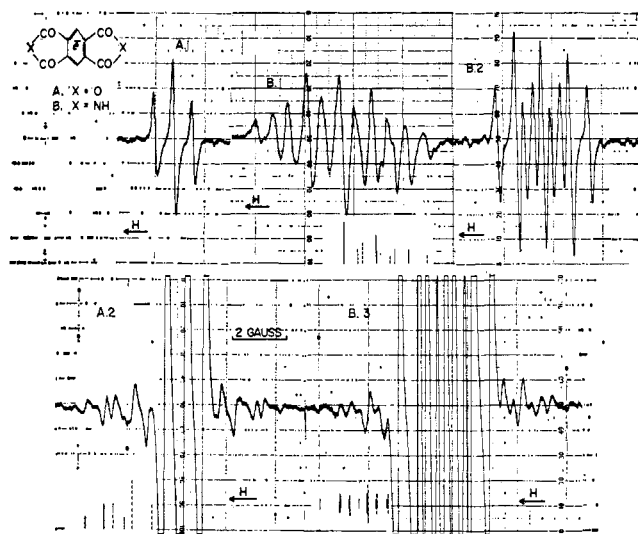


Figure 3. (A) (1) Derivative esr spectrum of the free radical anion of pyromellitic dianhydride at room temperature; (2) carbon-13 lines visible on amplification of the spectrum 1. (B) (1) Derivative esr spectrum of the free radical anion of pyromellitic diimide at lowered temperature; (2) the spectrum of the radical anion of pyromellitic imide anhydride; (3) carbon-13 lines visible on amplification of the spectrum 2.

C^{13} are visible. There are two groups of lines corresponding to splitting constants of 2.90 and 1.89 gauss. The lines corresponding to the smaller splitting constant have about twice the intensity of those associated with the larger splitting constant. The C^{13} satellites corresponding to the larger splitting constant have about 2.0% the intensity of the C^{12} lines. This is to be compared with a theoretical value of 2.2% based on the 1.108% natural abundance of C^{13} . This 1:2 intensity ratio of the C^{13} splittings can be explained if the larger of the two splittings is associated with the carbon at position 7 of the radical anion and the smaller one with the twice as numerous carbons in positions 1 or 8.

Pyromellitic Dianhydride. Electrolytic reduction of this compound at room temperature gives a triplet arising from splittings produced by two equivalent protons (Figure 3A1). At temperatures from 0 to -32° two other spectra were observed depending on the magnitude of the reduction potential. The first of these registered at 0° shows an additional splitting by a proton and the other an additional splitting by a group of two protons. C^{13} splittings of practically the same value as observed for pyromellitic diimide are visible at the extremes of the pyromellitic dianhydride anion spectrum. The intensity of the line corresponding to the smaller of the two C^{13} splittings is about 4.4% of the main line, which is in close agreement with theory.

Nitrophthalimides. The free radical anion of 3-nitrophthalimide is relatively unstable at room temperature, and measurements were made at temperatures ranging from -10 to -27° . The radical anion of 4-nitrophthalimide is much more stable, and strong esr signals were obtained at room temperature. The values of the splitting constants of the two anions are very similar (Table I) and can be interpreted in terms of an interaction between a nitrogen and three nonequivalent protons. The lines are broad (peak-to-peak width about 0.38 gauss) and probably cover small splittings of the atoms in the five-membered ring.

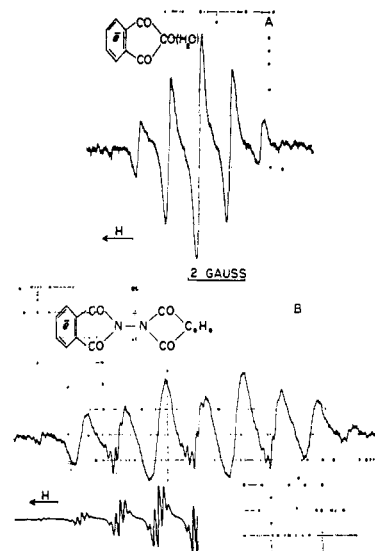


Figure 4. (A) Derivative esr spectrum of the free radical anion of triketohydrindene hydrate at -32° . (B) Derivative esr spectrum of the free radical anion of N-phthalimidophthalimide at -25° . The calculated spectrum using Lorentzian line shape and line width of 0.06 gauss is given below.

2-Phenyl-1,3-indandione and Triketohydrindene Hydrate. The esr spectra of the free radical anions of these two compounds have been studied because of a similarity of their structures to phthalimide. The indandione derivative gives an intense yellow color in dimethylformamide, and the esr spectrum of its radical anion measured at -42° consists of a broad triplet. Each of these lines is further split, possibly by five nearly equivalent protons. The lines overlap and are unsymmetrical, making the analysis difficult. The spectrum is given in Figure 2B, and an estimate of the splitting constants is tabulated in Table I.

The triketohydrindene hydrate anion gave a quintet for the esr spectrum both at room temperature and at -32° . This splitting presumably arises from four nearly equivalent protons (Figure 4A).

Naphthalic Imide and Anhydride. The anions of these compounds give intense spectra at room temperature although improved resolution was realized for the imide anion at -32° . Green colorations were produced around the cathode during electrolysis. The spectra are given in Figure 5 and the splitting constants are tabulated in Table I.

Discussion

Reduction Potentials. The free radical anions, whose esr spectra are reported in this investigation, were produced by electrolytic reduction at potentials of the first cathodic waves as given by the appropriate half-wave potentials. These data together with Tomeš's criterion¹⁰ and the MO energies of the first antibonding orbitals are tabulated in Table II.

Tomeš's criterion is a measure of the reversibility of an electrolytic process. For a one-electron reversible reduction, Tomeš has shown that the potential difference between the three-quarter and the one-quarter points on a reduction wave has a value of -55 mv at 20° . In the case of reduction of organic molecules,

(10) J. Tomeš, *Collection Czech. Chem. Commun.*, 9, 12, 81, 150 (1937).

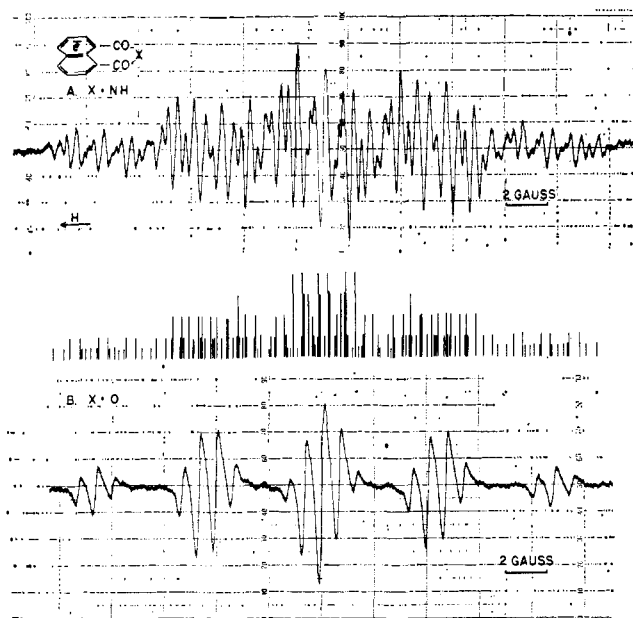


Figure 5. (A) Derivative esr spectrum of the free radical anion of naphthalic imide at -32° . The line-diagram reconstruction of the spectrum from splitting constants in Table I is given below. (B) Derivative esr spectrum of the free radical anion of naphthalic anhydride at room temperature.

the one-electron reversible process corresponds to the formation of free radical anions. It is evident from examination of the data in Table II that the values of $E_{3/4} - E_{1/4}$ are reasonably close to the expected value of -55 mv. Rieger⁶ has also determined the half-wave potentials of some of the compounds reported on here; however, comparison with our data is difficult because of the different references that were used.

Table II. Polarographic Data of the First Reduction Waves ($E_{1/2}$), Tomes's Criterion ($E_{3/4} - E_{1/4}$), and MO Energies in Terms of β_0 of the First Antibonding Molecular Orbital

Compound	$E_{1/2}$	$E_{3/4} - E_{1/4}$	MO energies
Phthalimide	-1.47	-0.062	0.5074
N-Phenylphthalimide	-1.37	-0.061	0.5074
N-Phthalimidophthalimide	-1.16	-0.051	0.5074
Pyromellitic diimide	-0.82	-0.066	0.3176
3-Nitrophthalimide	-0.84	-0.058	0.3255
4-Nitrophthalimide	-0.75	-0.066	0.2943
2-Phenyl-1,3-indandione	-1.18	-0.076	0.5074
Triketohydrindene hydrate	-0.97	-0.061	0.2497
Naphthalic imide	-1.25	-0.058	0.3967
Naphthalic anhydride	-1.12	-0.058	0.3967
Phthalic anhydride	-1.19	-0.062	0.5074
Pyromellitic dianhydride	> -0.5	...	0.3176

It has been reported by Maccoll,¹¹ Pullman, *et al.*,¹² Hoiijtink, *et al.*,¹³ and others^{14,15} that a simple relation exists between the half-wave potentials of one-electron reversible waves of aromatic compounds and

(11) A. Maccoll, *Nature*, **163**, 178 (1949).

(12) A. Pullman, B. Pullman, and G. Berher, *Bull. Soc. Chim. France*, **17**, 591 (1950).

(13) P. Balk, S. de Bruijn, and G. J. Hoiijtink, *Rec. Trav. Chim.*, **76**, 860 (1957).

(14) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

(15) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

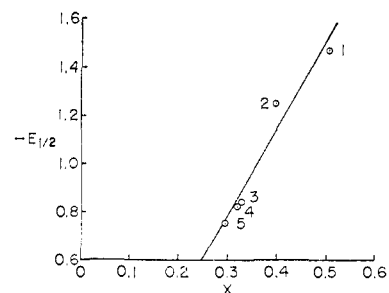


Figure 6. Plot of the dependence of the half-wave potentials of the first reduction waves of some of the compounds on energy of the first antibonding molecular orbital: (1) phthalimide, (2) naphthalic imide, (3) 3-nitrophthalimide, (4) pyromellitic diimide, (5) 4-nitrophthalimide.

the energy (expressed in terms of β_0) of the first antibonding orbital. A similar nearly linear relation seems to be present for the phthalimide derivatives, as is evident from Figure 6. Least-squares analysis of the data gives rise to the following equation

$$E_{1/2} = (0.28 \pm 0.04) - (3.56 \pm 0.11)x$$

where x is the MO energy of the first antibonding orbital (Table II). In the case of the phthalimides, the coefficient of x is somewhat higher than previously reported values¹³⁻¹⁵ of about 2.5.

The anhydrides, which have considerably lower half-wave potentials than the corresponding imides, are not included in this correlation even though both classes of compounds should have about the same energies for the first antibonding orbitals. These differences in the half-wave potentials suggest that other factors, such as entropy effects, associated with the electron transfer and solvation of the molecule and the ion, play a significant role in the process. Likewise, the N-substituted compounds do not fit the correlation. Here again, the first antibonding MO energies are similar to phthalimide, and the differences of the half-wave potentials are probably connected with the steric conditions of the electron-transfer process.

Esr Spectra Obtained on Reduction of Phthalimide.

Using a flow system and an electrolytic cell¹⁶ external to the esr spectrometer, Rieger⁶ observed three different esr spectra depending on the magnitude of the reduction potential. Two of the spectra were reproducible. One of these spectra, obtained at a potential not exceeding the potential of the second reduction wave of phthalimide, corresponded to an interaction of four nonequivalent protons and one nitrogen with splitting constants of 2.98, 1.89, 0.81, 0.31, and 0.78 gauss, respectively. The other reproducible spectrum, which was obtained at potentials in excess of the potential of the second reduction wave of phthalimide, corresponded to interactions of five nonequivalent protons and one nitrogen atom. The splitting constants were 2.4, 1.65, 0.6, 0.25, 0.1, and 1.3 gauss, respectively. The first of these spectra was attributed by Rieger to the phthalimide free radical anion in the enol form, although the phthalimide molecule is almost exclusively the keto form.¹⁷

(16) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

(17) A. E. Kellie, D. G. O'Sullivan, and P. W. Sadler, *J. Chem. Soc.*, 3809 (1956).

On reduction of phthalimide we have apparently obtained a single spectrum of different structure from those obtained by Rieger (see Figure 1A and Table I). We have attributed this spectrum to the anion of phthalimide in its keto form.

The observation of several free radical species on the reduction of phthalimide reported by Rieger, coupled with the instability of the radical anion of phthalimide at room temperature, can be explained as resulting from a reaction between the originally formed anion and the phthalimide molecule. A possible sequence of events, which would be compatible with this assumption, is the following.

The primarily formed free radical anion of phthalimide abstracts a proton from a nearby phthalimide molecule. The proton becomes attached to one of the oxygens of the radical anion (see Figure 7) and a low-stability neutral radical results, which would account for the second esr spectrum reported by Rieger. The five-proton splitting constants of this spectrum belong to the four nonequivalent protons of the aromatic ring and to the one attached to the nitrogen atom. The hydroxyl proton gives an unobservable splitting as is the usual observation. The calculated and experimental spin densities of this radical are listed in Table IV. This neutral radical can be transformed to the enolic form of the free radical anion of phthalimide by donating, as a proton, the hydrogen attached to the nitrogen atom. The occurrence of such a sequence of events is more probable in a flow apparatus where some time elapses between generation of the primary free radical and measurement in a nearby cavity. Our electrolytic apparatus of the *intra muros* type permits the simultaneous production of the free radical and observation of its esr spectrum.

Rieger, on the other hand, was able to observe the esr spectrum of the anion of phthalimide in its normal keto form on reduction of N-potassium phthalimide and of N-phthalimidophthalimide at potentials corresponding to the second polarographic waves. In the first case the radical anion is probably formed by abstraction of a proton from the solvent by a dinegative ion.⁶ The formation of the phthalimide free radical anion in the N-phthalimidophthalimide case probably results from the cleavage of the N-N bond of the dinegative ion and abstraction of a proton from the solvent. It is interesting to note that the splitting constants of nitrogen and the proton attached to it differ somewhat in the case of these two radicals. Our splitting constants for the phthalimide anion agree well with those given by Rieger for the radical produced from N-potassium phthalimide. Corresponding agreement is also realized in the two studies for the anions of phthalic anhydride, N-phthalimidophthalimide, pyromellitic diimide, and pyromellitic imide anhydride.

The esr spectrum of triketohydrindene hydrate anion was first measured by Adams, *et al.*¹⁸ They observed a spectrum of three overlapping sets of triplets and deduced two splitting constants of 1.95 and 1.59 gauss. For this supposedly same system, we observed a quintet (Figure 4) with a splitting constant of 1.07

(18) M. Adams, M. S. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

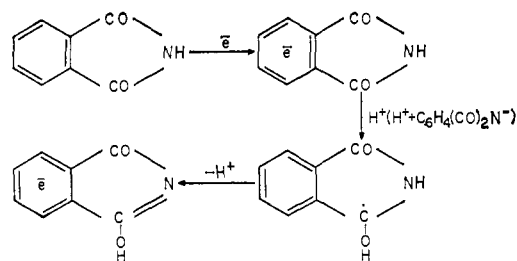


Figure 7. Transformation of the free radical anion of phthalimide.

gauss. Although it is possible that this quintet is not completely resolved, however, the reasons for the discrepancy between the two studies are not clear to us at this time.

Calculation of Unpaired Spin Densities. In order to associate the observed splitting constants with specific locations in the radical anion, Hückel and McLachlan¹⁹ MO calculations were conducted. For the heteroatoms in the radicals we have used the MO integral parameters as defined by Streitwieser,²⁰ and they are presented in Table III. The experimental spin densities were calculated from the McConnell equation:²¹ $a_i^H = Q_{CH^H} \rho_i$. The value of Q_{CH^H} was taken as -23.7 gauss.²² Comparison of the experimental and theoretical spin densities for some of the free radicals is given in Table IV. Good agreement was realized in most instances.

Table III. Molecular Orbital Parameters

Substituent	
>C=O	$h_C = -0.4$ $h_O = 2.0$ $k_{CO} = 1.6$
$\overset{C}{\underset{C}{>}}N^-$	$h_N = 1.2$ $k_{CN} = 1.0$
$\overset{C}{\underset{C}{>}}O$	$h_O = 1.2$ $k_{CO} = 1.0$
>CH-	$h_C = 1.2$ $k_{CC'} = 0.7$
$\overset{-}{\underset{C}{>}}OH$	$h_O = 2.0$ $k_{CO} = 1.0$

Evaluation of the experimental spin density on the nitrogen atom from its splitting constant is a more complicated task. Different investigators propose very different values of the parameter Q_N^N in the simple relation $a_N = Q_N^N \rho_N$. Actually, this simple formula should be substituted by a more complex relation $a_N = Q_{N(C,H)}^N \rho_N + Q_{CN}^N (\rho_C + \rho_C')$ ²³ analogous to that for C^{13} ,²² since the splitting caused by the nitrogen is dependent on the unpaired spin densities on the nitrogen atom and on the neighboring carbon atoms. Several authors have found that a value of about 30 gauss²³⁻²⁵ is suitable for the first constant, $Q_{N(C,H)}^N$.

(19) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(20) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 117.

(21) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(22) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

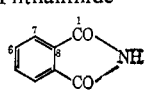
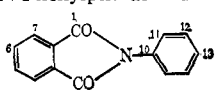
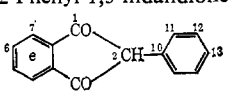
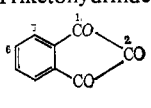
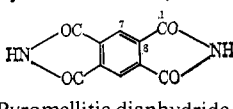
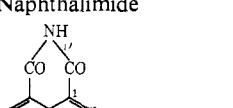
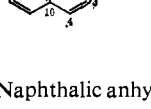
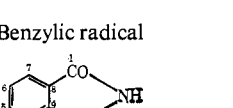
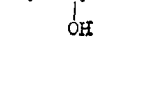
(23) B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 1455 (1964).

(24) E. W. Stone and A. H. Maki, *ibid.*, **39**, 1635 (1963).

(25) N. M. Atherton, F. Gerson, and J. N. Murrell, *Mol. Phys.*, **5**, 509 (1962).

However, there exists much disagreement on the value of the second constant, Q_{CN}^N , and values ranging from -2 to 8 were proposed.²³⁻²⁶

Table IV. Calculated and Experimental Spin Densities

Radical anion	Position	Spin density			
		Hückel	Calcd McLachlan	Exptl	
 Phthalimide	O	0.063	0.054	...	
	N	0.000	-0.020	0.014 ^a	
	1	0.153	0.174	...	
	6	0.101	0.107	0.112	
	7	0.025	-0.012	0.012	
	8	0.158	0.187	...	
	Phthalic anhydride	6	0.101	0.107	0.113
		7	0.025	-0.012	0.011
 N-Phenylphthalimide	O	0.063	0.054	...	
	N	0.000	-0.017	...	
	1	0.153	0.174	...	
	6	0.101	0.108	0.109	
	7	0.025	-0.012	0.014	
	8	0.158	0.187	...	
	10	0.000	0.001	...	
	11	0.000	-0.002	0.014	
	12	0.000	0.000	...	
	13	0.000	-0.002	0.014	
	 2-Phenyl-1,3-indandione	O	0.063	0.053	...
		1	0.154	0.174	...
		2	0.000	-0.012	...
6		0.101	0.108	0.109	
7		0.025	-0.012	0.013	
10		0.000	0.000	...	
11		0.000	-0.002	0.013	
12		0.000	0.000	...	
13		0.000	-0.002	0.013	
 Triketohydrindene hydrate		O(1)	0.065	0.058	...
		1	0.129	0.146	...
		O(2)	0.157	0.136	...
		2	0.311	0.343	...
	6	0.024	0.018	0.045	
	7	0.037	0.040	0.045	
	8	0.011	-0.001	...	
	O	0.048	0.041	...	
 Pyromellitic diimide	N	0.000	-0.014	...	
	1	0.109	0.123	...	
	7	0.005	-0.036	0.030	
	8	0.140	0.170	...	
 Pyromellitic dianhydride	7	0.005	-0.036	0.030	
	O	0.028	0.022	...	
 Naphthalimide	N	0.000	-0.010	0.011 ^a	
	1'	0.064	0.067	...	
	1	0.091	0.078	...	
	2	0.120	0.153	0.146	
	3	0.027	-0.023	0.024	
	4	0.170	0.239	0.176	
	9	0.000	-0.017	...	
	10	0.000	-0.045	...	
	 Naphthalic anhydride	2	0.120	0.153	0.153
		3	0.027	-0.023	0.025
4		0.170	0.239	0.177	
 Benzylic radical		O(1)	0.063	0.053	...
	O(3)	0.063	0.046	...	
	N	-0.021	-0.019	0.003 ^a	
	1	0.063	0.053	...	
	3	0.323	0.399	...	
	4	0.061	0.057	0.070	
	5	0.045	0.025	0.025	
	6	0.091	0.109	0.101	
	7	0.017	-0.021	0.011	
	8	0.114	0.145	...	
9	0.076	0.068	...		

^a Calculated from the splitting of attached proton.

(26) J. C. M. Henning and C. de Waard, *J. Chem. Phys.*, **35**, 2258 (1961).

Judging from the agreement in the literature, a more reliable approach to evaluating the spin density on the nitrogen atom is to use the splitting of the hydrogen atom attached to it. This has a form $a_{NH}^H = Q_{NH}^H \rho_N$, which is analogous to McConnell's formula for the C-H bond. A value for Q_{NH}^H of -33.7 gauss has been proposed.²³ The nitrogen spin densities have been arrived at using this procedure, and good agreement with the McLachlan spin densities is realized (Table IV).

The first antibonding orbital in phthalimide has a node at the nitrogen position; consequently, this position has a very low spin density in the free radical anion. Another consequence of the presence of this node is that changes in the Coulomb integral of the nitrogen will have little effect on the spin densities in the rest of the molecule or on the energy of the first antibonding orbital. This conclusion seems to be supported by the results obtained on N-phenylphthalimide. There appears to be little interaction between the two parts of the molecule since the splittings of the phthalimide part are practically unchanged by the substitution of a phenyl group on the nitrogen (Table I). An analogous situation should exist in the case of N-phthalimidophthalimide radical anion if it were not for the possibility of electron exchange. The esr spectrum of this anion is composed of nine broad lines (Figure 4B) which can be attributed to an interaction of four equivalent protons and a pair of equivalent nitrogens. The values of the splitting constants are approximately one-half of those of phthalimide (Table I). Such spectra can be interpreted as resulting from fast exchange between the two symmetrical parts of the molecule. The exchange frequency should be considerably greater than that of the hyperfine interaction, i.e., 10^7 sec⁻¹. Examples of such electron exchanges have been reported in the literature previously.^{27,28}

C¹³ Splittings. The esr spectra of the pyromellitic dianhydride and of the pyromellitic imide anhydride free radical anions (Figure 3) show distinct C¹³ splittings. There are two distinct splitting constants with practically the same values for both anions. From the relative intensities of the C¹³ lines, the larger splitting constant (2.90 gauss) is attributed to position 7 of radical anions and the smaller one (1.89 gauss) to positions 1 or 8.

Karplus and Fraenkel²² showed that the C¹³ splitting depends strongly on the spin density of the neighboring atoms and is given by the relation

$$a^C = (S^C + \sum_{i=1}^3 Q_{CX}^C) \rho^\pi + \sum_{i=1}^3 Q_{XC}^C \rho_i^\pi$$

S and Q are the σ - π polarization constants, and the ρ^π 's are the spin densities on the carbon ρ^π and its neighbors ρ_i^π .

Using this formula and the polarization constants given in the literature,^{22,24,29} we have attempted to locate the position responsible for the C¹³ splitting and to check the consistency of the theory with our results. The constants used (in gauss) are $S^C = -9.8$, $Q_{CC}^C = 14.44$, $Q_{C'C}^C = -13.94$, $Q_{CO}^C =$

(27) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6462 (1958).

(28) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 779 (1963).

(29) M. R. Das and G. K. Fraenkel, *ibid.*, **42**, 1350 (1965).

17.7, $Q_{OC}^C = -27.1$, and $Q_{NC}^C = -20.5$. Spin densities as calculated by the McLachlan method (Table IV) were used. The calculated C^{13} splittings were -5.9 , 2.0 , and 0.1 gauss for positions 7, 8, and 1, respectively. The largest splitting is predicted for position 7 and this was confirmed experimentally; however, the calculated value was twice as big as the observed one. These results therefore suggest that the splitting constant of 1.89 gauss is associated with position 8 rather than 1. The results of these calculations, although in qualitative agreement with the experimental data, should be treated with some reserve, since it has been pointed out by Karplus and Fraenkel²² that the calculated C^{13} splittings are very sensitive

functions of the spin density of a central atom and of its neighbors, and cancellations can occur among different contributions to the splitting. In addition, Das and Fraenkel²⁹ showed that calculated spin densities adjusted to fit the proton splittings are not always accurate enough for "blank positions" where no proton is attached.

Acknowledgment. We wish to acknowledge our appreciation to Professor G. K. Fraenkel for bringing Dr. Rieger's thesis to our attention and to Professor Rieger for permission to quote some of his results. We also thank Professor A. H. Maki for a copy of his SESRS computer program and Mr. D. Saperstein for his help in preparation of some of the computations.

Basicities of Methanol and 2-Propanol as Determined by Raman Spectrophotometry¹

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Abstract: Raman intensity measurements have been used to determine the concentration of unprotonated alcohol in solutions of methanol in aqueous hydrochloric acid and 2-propanol in aqueous perchloric and hydrochloric acids. This technique leads to the following values of H_0 for 50% protonation: methanol in HCl, -4.86 ± 0.37 ; 2-propanol in HCl, -4.72 ± 0.95 ; 2-propanol in HClO₄, -5.16 ± 0.45 .

It has always been difficult to determine the basicities of aliphatic alcohols; they are too weakly basic for the techniques used in dilute aqueous solutions, and they do not have the usual spectral properties which have been used to measure base strengths of other compounds in concentrated acid solutions.³ Moreover, the study of aqueous solutions of alcohol is complicated by the similarity in chemical and physical properties of the solute and solvent.

It is not surprising, then, that the first quantitative evidence for protonation of a simple alcohol appears to have been obtained indirectly from a kinetic study primarily concerned with another reaction.⁴ In their studies of the rate of hydride transfer from 2-propanol to the triphenylcarbonium ion, Bartlett and McCollum⁴ attributed the decrease in rate produced by increasing acid concentration to the formation of an oxonium ion. Their results indicated a value of -3.2 for the pK_{BH^+} of 2-propanol. (The pK_{BH^+} is defined as the value of H_0 for which the ratio $(BH^+)/ (B) = (ROH_2^+)/ (ROH)$ is unity.) Similar kinetic evidence has been obtained for 2-propanol in the oxidation by chromium(VI) oxide⁵ ($pK_{BH^+} = -3.8$) for ethanol in a hydride-transfer reaction⁶ ($pK_{BH^+} = -2.3$), and for *t*-butyl

alcohol in the alkylation of acrylonitrile⁷ ($pK_{BH^+} = -3.8$). All these systems were studied as relatively dilute solutions of alcohol in concentrated acid, as is evident from the pK values. (For example, 50% sulfuric acid has an H_0 of -3.4 .)

In addition to measurements based on kinetic techniques, more direct equilibrium studies have been carried out, using the phase distribution of alcohol between aqueous acids and organic solvents or pure alcohol. These methods indicated that 2-propanol had a pK_{BH^+} of around -1.2 ,⁸ in contradiction to the result from the kinetic method. On the other hand, similar experiments by Arnett and his group⁸ and by Deno and co-workers⁹ tended to confirm the original estimates of Bartlett and McCollum for the basicity of simple alcohols. Further conflicting evidence was offered by an nmr study of ethanol,¹⁰ which indicated 50% protonation at an H_0 value of -4.8 , but did not give the expected dependence of the chemical shift on the acidity function.

In view of the difficulties of measuring the basicity of alcohols, and the contradictory data for them, a new technique proposed by Deno and Wisotsky¹¹ is of great interest. They measured the Raman intensity of

(1) This research supported by the U. S. Atomic Energy Commission.

(2) Max-Planck-Institut für Chemie, 6500 Mainz, Germany.

(3) Cf., for example, E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

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