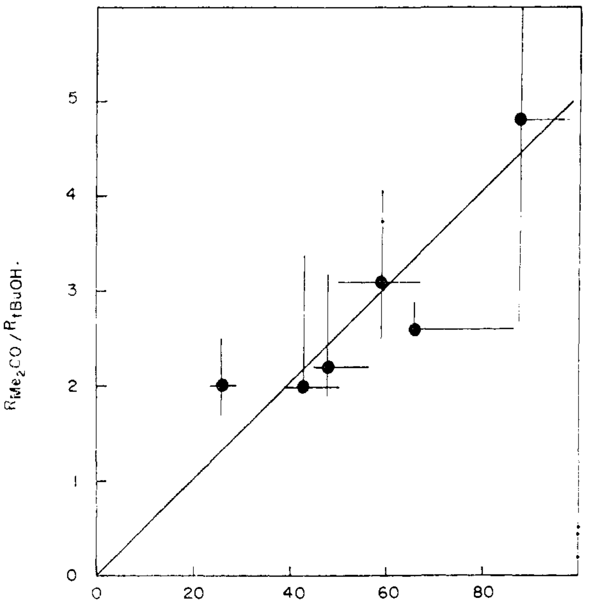

Fig. 3.—Plot of $R_{Me_2CO}/R_{t\text{-}BuOH}$ *vs.* $1/(R_{MeOH})^{1/2}$; the slope of the plot is theoretically equal to the rate function $k_4k_{10}^{1/2}/k_8$.

with the extrapolation of higher temperature thermal data for reaction 4 obtained by other workers. With similar assumptions concerning the rate constants for radical reactions, Hinshelwood's data from the pyrolysis of di-*tert*-butyl peroxide-nitric oxide mixtures at 160° suggest $k_4 \cong 21$ sec.$^{-1}$ at 25°.[21] Batt and Benson's[19] thermal data for di-*tert*-butyl peroxide decomposition in the 130–160° temperature range give $k_4 \cong 27$–97 sec.$^{-1}$ at 25°. In view of the approximations and uncertainties involved in the present estimate and the estimates from the Hinshelwood's and Batt and Benson's data, the agreement is satisfactory and adds credence to the reaction mechanism suggested here. Data for reaction 4 based on photochemical decomposition of di-*tert*-butyl peroxide lead to values for k_4 at 25° which are about 10^2 to 10^3 times higher than those from thermal experiments; this may be the result of fragmentation of non-thermally equilibrated radicals formed in the primary act.[22,23]

Our mechanism has not incorporated the reaction 18 which was suggested recently by Hoare and Wellington in explanation of di-*tert*-butyl peroxide thermal and photodecompositions in the 50–135° temperature range.[24] Reaction 18 cannot be im-

$$(CH_3)_3CO + O_2 \longrightarrow (CH_3)_3COO_2 \longrightarrow CH_3O_2 + CH_3COCH_3 \quad (18)$$

portant in this system at 25° since the ratio $R_{Me_2CO}/R_{t\text{-}BuOH}$, column 12 of Table I, is invariant with change in O_2 pressure from 19 to 740 mm.; compare values for runs 5, 10 and 11. If 18 were important here a dramatic change in this ratio would be expected. If association between alkoxyl radicals and oxygen occurs, it must involve a very weak interaction at room temperature since the ultimate fate of the radicals is not altered by oxygen pressure variation.

Acknowledgment.—The authors gratefully acknowledge the support of this work by the United States Public Health Service, National Institutes of Health, Bethesda, Md.

[21] C. N. Hinshelwood, *Chem. Soc.* (*London*) *Spec. Publ.*, **9**, 49 (1957).

[22] D. H. Volman and W. M. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953).

[23] G. R. McMillan, *ibid.*, **82**, 2422 (1960).

[24] D. E. Hoare and C. A. Wellington, "Eighth Symposium on Combustion," Williams and Wilkins Co., Baltimore, Md., 1962, p. 4.

[Contribution from the Instrument Division, Varian Associates, Palo Alto, California and the Department of Chemistry, University of Kansas, Lawrence, Kansas]

Electron Paramagnetic Resonance of Aromatic and Aliphatic Nitro Anions in Aqueous Solution[1]

By L. H. Piette, Peter Ludwig and Ralph N. Adams

Received April 16, 1962

A wide variety of aromatic and aliphatic nitro anion radicals can be generated in aqueous media. The lifetimes are reasonably long. The e.p.r. spectra can be interpreted with ease in most cases. One of the most significant findings is that a relatively large solvent effect on the N^{14} coupling constant exists for the aromatic compounds, whereas it is absent in the spectra of the aliphatic compounds.

The properties of aromatic nitro anion radicals generated electrochemically in acetonitrile have been dealt with thoroughly by Geske and Maki.[2,3] Recently it was reported that both aromatic and aliphatic nitro anion radicals could be generated in ordinary aqueous media[4]. We wish to summarize the aspects of the aqueous solution results which are of interest in electron paramagnetic resonance (e.p.r.) studies. Details of the electrogeneration technique in aqueous media are given elsewhere.[5]

Experimental

All e.p.r. studies were carried out with a Varian V-4500 spectrometer employing 100-kc. field modulation. The cells for electrogeneration were rectangular Varian cells with an inner thickness of *ca.* 0.5 mm. Generations were performed

[1] Based on material presented at the 140th American Chemical Society meeting, Chicago, September 1961.

[2] D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

[3] (a) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960). (b) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

[4] L. H. Piette, P. Ludwig and R. N. Adams, *ibid.*, **83**, 3909 (1961).

[5] L. H. Piette, P. Ludwig and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962).

TABLE I

COUPLING CONSTANTS OF SUBSTITUTED NITROBENZENE ANIONS IN AQUEOUS SOLUTION[a]

Compound[b]	a_N	a_1	a_2	a_3	a Remarks
Nitrobenzene	13.87	3.52[c]	3.30[d]	1.12[d]	
Nitroanilines					
para	15.30	3.36	1.12[f]	1.12[g]	
ortho-	14.50	3.25[d]			
meta-	13.36	3.3[d]			
Nitrophenols					0.1 *M* LiOH as supporting electrolyte
para-	14.60	3.1[d]	0.7[d]		
ortho-	14.63	3.6[d]	0.6[d]		
meta-	14.78	3.3[e]	0.95[e]		
p-Nitroanisole	14.48	3.31[d]	1.01[d]	0.32[e]	5% *1*-propanol for solubility
p-Nitrobenzoic acid	12.79	3.32[d]	2.23[d]		40% *1*-propanol for solubility
3-Nitro-*o*-phthalic acid	13.74	3.79[d]	0.60[e]		0.1 *M* KOH supporting electrolyte
1-Nitro-2,4,6-trimethylbenzene	19.21	..	..		

[a] Supporting electrolyte 0.1 *M* KCl unless otherwise noted; absolute value of coupling constants in gauss, a_N is coupling constant of nitro group. [b] Concentration of all nitro compounds *ca.* 1 m*M*. [c] Interaction with a single proton. [d] Interaction with 2 equivalent protons. [e] Interaction with 3 equivalent protons. [f] Interaction with 4 equivalent protons [g] Due to interaction with second N^{14} nucleus (amino nitrogen).

at the usual mercury pool surface. All solutions were prepared from reagent grade chemicals and aromatic nitro compounds were Eastman white label grade or purified by conventional means. The aliphatic nitro compounds were graciously supplied by Commercial Solvent Corporation, New York, and were used without further purification.

All solutions were thoroughly deaerated before electro generation. The applied potentials, ranging from −0.3 to −2.0 v. *vs.* s.c.e. were selected on the basis of polarographic studies of the particular compounds.

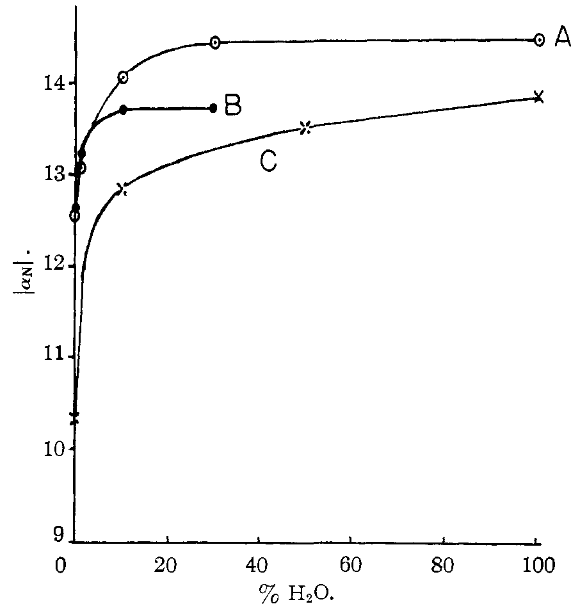

Fig. 1.—Solvent dependence of $|a_N|$ for acetonitrile–water mixtures: A, *p*-nitroaniline anion; B, *o*-nitroaniline anion; C, nitrobenzene anion (coupling constant in gauss).

Hyperfine coupling constants were measured by careful comparison with the splittings of a fresh solution of peroxylamine disulfonate. The value of 13.00 gauss was taken for the peroxylamine splitting.[6] Recorded coupling constants are the average of usually 2 or 3 spectra. In an attempt to eliminate sweep non-linearity, all spectra and calibrations were recorded from both ends of the field and the average used for coupling constant calculations. The precision of the coupling constants is believed to be ± 0.02 gauss. No measurements of *g* values were made.

Results and Discussion

1. **Aromatic Nitro Compounds.**—In common with the findings of Maki and Geske, many of the anion radicals in aqueous solution show a dominant N^{14} coupling. Interpretation of such spectra is straight forward. In assigning ring proton couplings it was assumed that the coupling with ortho protons would be stronger than with meta. Individual spectra are discussed as required below and the absolute values of the various couplings are listed in Table I. Since there are no unusual characteristics, individual aromatic nitro anion spectra are not shown.

2. **Solvent Effects on Coupling Constants.**—It is important to point out that coupling constants of the aromatic nitro anions show a marked solvent dependence. This is seen in Fig. 1 where the $|a_N|$ coupling for nitrobenzene, *o*-, and *p*-nitroaniline is plotted for the solvent system acetonitrile–water. (In molecules where two N^{14} couplings are possible, discussion of the N^{14} coupling means that from the nitro group unless otherwise noted). The effect is very pronounced for small amounts of water and amounts to about a 40% change of $|a_N|$ for nitrobenzene. The dependence of proton couplings is less striking but can, on the other hand, account for marked changes in the overall spectrum. Thus nitrobenzene anion in acetonitrile shows *ortho* and *para* proton couplings of 3.39 and 3.97 gauss, respectively. The entire spectrum in acetonitrile consists of 54 hyperfine lines.[2] From Table I it can be seen that the *para* and *ortho* couplings are much closer in magnitude in water than in acetonitrile. Thus, with certain mixtures of acetonitrile–water, or under only moderate resolution, the e.p.r. spectrum shows only 36 lines. This corresponds to a triplet from the N^{14}, split into a quartet by 3 *apparently* equivalent protons (2 *ortho* + *para*), and then further split into triplets by the 1.12 gauss meta coupling. By varying the acetonitrile–water ratio (in the low water content region) it is possible to realize variations between *apparent* 36 and 54 line spectra depending on the overlaps and varying resolution. A more quantitative treatment of solvent effects on coupling constants will be given soon.

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(6) J. Townsend, S. I. Weissman and G. E. Pake, *Phys. Rev.*, **89**, 606 (1953).

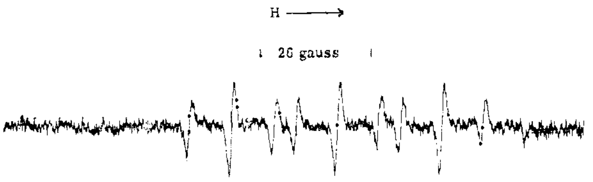


Fig. 2.—E.p.r. spectrum of 1-nitropropane anion in aqueous solution.

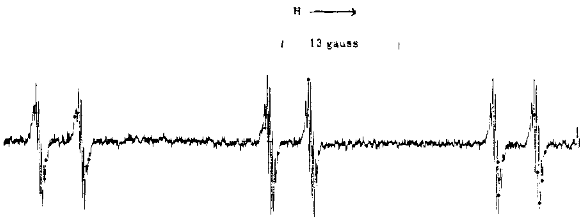


Fig. 3.—E.p.r. spectrum of 2-nitropropane anion in aqueous solution.

3. Interpretation of Aromatic Nitro Anion Spectra. a. Nitroanilines.—With the exception of the *ca.* 3 gauss increase in N^{14} coupling, the e.p.r. spectrum of the *p*-nitroaniline anion radical is identical with that reported by Maki and Geske in acetonitrile.[3b] (The multiplets of 13 lines show further resolution in acetonitrile which contains small amounts of water.) Only the splittings for one N^{14} and one pair of equivalent protons can be measured for ortho and metal nitroaniline anions due to the relatively poor quality of the spectra.

b. Nitrophenols.—It is apparently not possible to obtain the anion radicals of nitrophenols in acetonitrile. Also these anion radicals are not obtained in acidic aqueous solution but are readily generated above about pH 7. This suggests the radical anion can be generated only from the phenolate ion. This point is ambiguous since a rapid reaction of the nitrophenol anion with protons in acid solution could lead to the same effect.

Obviously the three ring protons in *m*-nitrophenol cannot be equivalent. The apparent equivalence of these protons in the e.p.r. spectrum of the *m*-nitrophenol anion is certainly due to lack of resolution of closely spaced lines. One can rationalize three *nearly* equivalent protons on the following basis: the inductive effect of a strong meta directing group like the nitro function is partially compensated by the *ortho-para* influence of a phenol function *meta* to the nitro group. Such classical arguments of organic chemistry are in qualitative agreement with a large number of e.p.r. spectra of aromatic radical ions. Similar arguments can be applied to the *o*-nitrophenol spectrum which shows interaction of the unpaired electron with two pairs of identical protons.

c. Nitrocarboxylic Acids.—Neither *p*-nitrobenzoic acid nor the 3-nitro-*o*-phthalic acid give anion radicals in acetonitrile or acidic aqueous media. E.p.r. spectra of these compounds were obtained only in basic aqueous solution. With *p*-nitroanisole, having no ionizable proton on the oxygen, e.p.r. spectra are obtained both in acetonitrile or aqueous media.

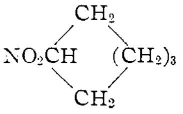
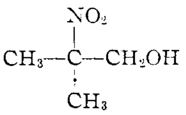
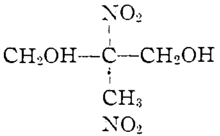
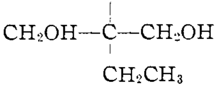
4. Aliphatic Nitro Anions.—The e.p.r. spectra of the negative ions of aliphatic nitro compounds are distinguished by their simplicity. The strongest coupling results from the isotropic interaction of the magnetic moments of the unpaired electron and the N^{14} nucleus as indicated by the dominant N^{14} hyperfine structure of all spectra. Further hyperfine splittings result from interactions with protons very close to the nitro group.

The apparent lifetime of the aliphatic anions is of the order of 0.5 sec. As would be expected they are considerably less stable than their aromatic counterparts.

The coupling constants are listed in Table II. Since only those protons on carbons adjacent to or at most one carbon removed from the nitro function produce hyperfine interaction, all of the compounds can be discussed in three general groups.

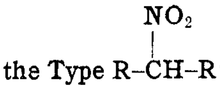
TABLE II

COUPLING CONSTANTS OF ALIPHATIC NITRO ANIONS IN AQUEOUS SOLUTION[a]

Compound	a_N	$a_{H(CH_2)}$		
$CH_3CH_2NO_2$	25.5	9.75		
$CH_3CH_2CH_2NO_2$	24.8	9.98		
$CH_3CH_2CH_2CH_2NO_2$	24.2	9.76		
$CH_3(CH_2)_4CH_2NO_2$	25.1	10.1		
	a_N	$a_{H(CH)}$	$a_{H(CH_3)}$	$a_{H(CH_2)}$
$CH_3CHNO_2CH_3$	25.2	4.60	0.24	0.12
$CH_3CHNO_2CH_2CH_3$	24.7	3.19		
	25.7	5.65		0.8
	a_N	$a_{H(CH)}$		
$CH_3CH_2CHNO_2CH_2OH$	24.7	3.26		
	a_N			
 $CH_3-\underset{CH_3}{\overset{NO_2}{C}}-CH_2OH$	23.8			
 $CH_2OH-\underset{CH_3}{\overset{NO_2}{C}}-CH_2OH$	25.5			
 $CH_2OH-\underset{CH_2CH_3}{\overset{NO_2}{C}}-CH_2OH$	24.9			

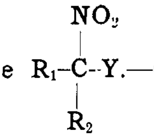
[a] Solvent system 0.1 *M* KCl with 10% *N*-propanol to aid solubility; absolute value of coupling constant in gauss.

(a) Compounds of Type $R-C^1H_2-NO_2$.—Here the strong N^{14} triplet is split further by the two protons on the C^1 carbon into a further triplet. A typical spectrum is seen in Fig. 2. In the case of nitromethane only a transient and very weak signal was observed which did not allow determination of the splittings. All spectra showed a triplet hydrogen splitting (*i.e.*, from 2 equivalent protons)—hence, there is no evidence of the so-called *aci*-form $R-CH=NO_2^-$ (which necessarily would give a doublet) although the anions were generated in alkaline or unbuffered media.


$R\text{–}\overset{NO_2}{\overset{|}{CH}}\text{–}R'$

(b) Compounds of the Type R–CH–R′.—Figure 3 shows the spectrum of 2-nitropropane which is representative of this group of compounds. The N^{14} triplet is split into a doublet from the single proton on the carbon containing the nitro group. The additional but much smaller splittings are due to the adjacent methyl (or, in other compounds, methylene) protons. Again, interaction with protons on carbons more than two removed from the nitro group are not observed.

In nitro cyclohexane one finds the dominant N^{14} coupling, a rather strong doublet splitting from the single hydrogen and a further quintet which must be interpreted as derived from two pairs of *approximately* equivalent protons. No assignment of the latter can be made at present. Nitro cyclopentane yielded only a very weak and unresolved e.p.r. spectrum.


$R_1\text{–}\overset{NO_2}{\underset{R_2}{C}}\text{–}Y$

(c) Compounds of the Type R₁–C–Y.—Compounds of this type, as exemplified by the last three alcohols in Table II show only a N^{14} coupling. This is true whether R_1 is CH_3 or a second alcohol group as in the diols. The spectra resemble the peroxylamine disulfonate spectrum- the only essential difference is $|a_N|$ is about twice as large as that of the peroxylamine.

Other compounds with Y = Cl, NO_2 show no evidence of anion radical formation. Compounds from which no spectra were obtained include 1-chloro-1-nitro propane, 2-chloro-1-nitro propane, 1-chloro-1-nitro ethane, and 2,2-dinitropropane. It is surprising that the last named compound gave no signal since tetranitromethane as well as dinitro methane gave well resolved spectra. In the latter two cases, the radical ions are quite unstable (as well as the starting materials) and the spectra may be composed of several structures.

Finally, the N^{14} coupling constants in aliphatic compounds (*ca.* 25 gauss) is much larger than in the corresponding aromatic nitro anions. Contrary to the results with aromatics practically no solvent effect on the N^{14} coupling could be found with the aliphatic anions. It has been pointed out by Geske and Ragle[7] that the value of $|a_N|$ in an aromatic nitro anion approaches that of the aliphatic counterpart when the nitro group is twisted out of the plane of the benzene ring by steric effects of bulky substituents. In the present study one notes this "aliphatic behavior" for nitromesitylene reflected in the magnitude of $|a_N|$.

Acknowledgments.—This work was supported by the Air Force through the Air Force Office of Scientific Research and by the Atomic Energy Commission through contract AT(11-1)-686. This support is gratefully acknowledged.

(7) D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

The Thermal Unimolecular Isomerization of Methyl Isocyanide. Fall-off Behavior[1]

BY F. W. SCHNEIDER AND B. S. RABINOVITCH

RECEIVED JUNE 15, 1962

The thermal unimolecular isomerization of methyl isocyanide to acetonitrile has been investigated as part of a continuing thorough investigation of this reaction type. Fall-off has been studied at three temperatures, and in one case (230°) extends over the range of k/k_∞ from 1.00 down to 0.0016. Activation energies have also been determined over a wide range of fall-off ($A_\infty = 10^{13.6}$, $E_a(\infty) = 38.4$ kcal./mole). The data has been treated on the basis of RRKM theory; results which justify the assumptions made in the theory with regard to intramolecular and intermolecular energy exchange are summarized. Accurate evaluation of the quantum statistical summation of the harmonic vibrational energy levels involved in the theory is made. Additional values of the semi-classical approximation correction factor a are given. The vibrational patterns employed are essentially the full set for the molecule and activated complex, rather than the empirical approximation of a single degenerate oscillator model or similar elaborations not directly related to the actual vibrational patterns. The agreement of theory with experiment is very satisfactory. Some further comparisons and assessment of the quantum statistical formulation of unimolecular reactions are given. The calculations are extended to the quantitative inclusion of anharmonicity effects, and evaluation of the role and importance of such factors. Governed by the uncertainty of the correction, anharmonicity effects appear to raise the low pressure rate by 25–40%. An overall figure axis rotation is also taken as active and its effect on the calculated behavior determined.

In the forty years since the formulation of the Lindemann–Christiansen–Hinshelwood mechanism of unimolecular reactions, much experimental work has been done to test this scheme and alternative assumptions and approximations regarding each step. It is remarkable, however, that with the possible exception of N_2O_5[2] there is still no example of a reaction system whose study approaches completeness. Such a study ideally should include fall-off data from the high to low pressure limits at several temperatures, and determination of the activation energy variation over this range; the study of various inert gas efficiencies in activation–deactivation over the fall-off region, and especially at the low pressure end; the study of the effect of variation of molecular parameters, as by variation of molecule chain

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(1) Presented at the Symposium on Elementary Reactions, Am. Chem. Soc., St. Louis, Mo., March, 1960, and Washington Meeting, March, 1962, Am. Chem. Soc. Abstracted in part from the Ph.D. Thesis of F. W. S., University of Washington, 1962. This work was supported by the National Science Foundation.

(2) R. L. Mills and H. S. Johnston, *J. Am. Chem. Soc.*, **73**, 938 (1951), and a number of succeeding papers; references to the older literature on this reaction are given.