The Compatibility of Free-Radical and Peroxide Functional Groups

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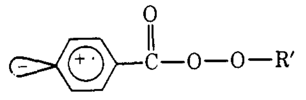
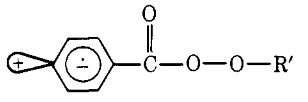
Abstract: A series of radical-substituted benzoyl peroxides and *tert*-butyl peresters have been generated by bromination of the benzylic side chain with *N*-bromosuccinimide. In all cases but one the reaction gave the corresponding α-brominated peroxides in good yield and without any detectable intramolecular radical-induced decomposition of the peroxide functional group.

Molecules containing both a free radical and a peroxidic functional group are of interest because of their occurrence in peroxide-initiated reaction mixtures. The radical peroxides in this paper were chosen because they might have functioned as intermediates in a radical-induced decomposition of the corresponding peroxides and also because of their resemblance to other radicals that have been postulated as intermediates in the induced decomposition of benzoyl peroxide.[1-4] The fate of the peroxide group indicates whether or not the radical is likely to be an intermediate in the induced decomposition reaction. Not all of the species that have been proposed as intermediates in the decomposition of benzoyl peroxide can be studied in this way, but the behavior of the accessible, structurally related radical peroxides is of some relevance to the problem.

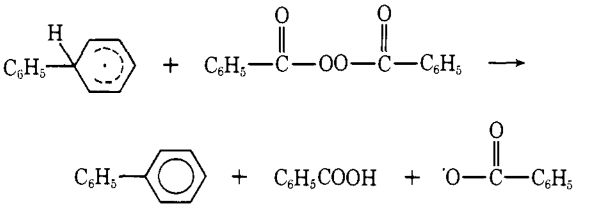
In an earlier communication[5a] we noted that bis(*p*-iodobenzoyl) peroxide exchanges iodine for chlorine in a reaction in which a σ radical intermediate abstracts chlorine from CCl_4 solvent. The failure of the peroxide functional group to decompose either during the formation of the σ radical or during its subsequent lifetime, even though the lifetime is brief, eliminates that radical as an intermediate in the induced decomposition of benzoyl peroxides. This is not particularly surprising since the radical probably has a σ ground state and would require activation to one of the π states I or II in order to interact effectively with the peroxidic functional group.[6]

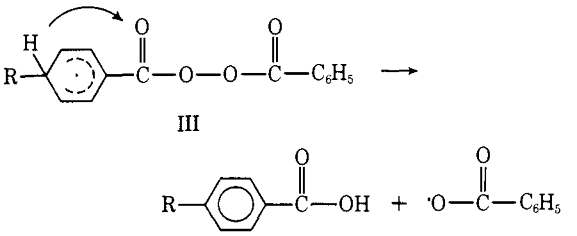

I


II

When the *p*-iodo peroxide or bis(*m*-iodobenzoyl) peroxide is decomposed at 115–130° in the field of an nmr spectrometer, CIDNP is observed from the protons of the *p*- or *m*-diiodobenzene product. No peroxide CIDNP signal could be detected although the chemical evidence[5] leaves no doubt that chloro- and probably iodo-substituted peroxides are formed (or re-formed) from the σ radical peroxide.[7,8]

π **Radicals.** Mechanisms for the radical-induced decomposition of benzoyl peroxide can be divided into three categories, direct homolytic displacement on a peroxidic oxygen,[9-11] reactions in which a bond is formed between the attacking radical and an ortho or para carbon atom,[4,12,13] and reactions in which the peroxide group is reduced by transfer of a hydrogen atom from the radical (eq 1).[12] It is possible that the latter two categories are related, because one way for a radical attacking the ring to bring about decomposition of the peroxide is by intramolecular transfer of a hydrogen atom (eq 2). It is well established that the reaction


(1)


III

(2)

subsequent to the bonding of R· to the ring is *intra*-molecular and that the hydrogen atom is donated to the closer of the two acyloxy moieties, the other undergoing extensive decarboxylation.[2a,2b]

An alternative to the Cadogan mechanism (eq 2) is the concerted formation of a hypothetical intermediate lactone IV plus a benzoyloxy radical, a mechanism proposed by Walling.[3,4] The high reactivity of the

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(1) D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, **78**, 4296 (1956).

(2) (a) J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965). (b) It should also be noted that there are no known instances in which a benzoyl peroxide is decomposed by the attack of a radical on a ring position occupied by anything but hydrogen.

(3) C. Walling and Z. Čeković, *J. Amer. Chem. Soc.*, **89**, 6681 (1967). The lactone is postulated to act as a precursor for both the acid RC_6H_4-COOH and the hydrocarbon RC_6H_5.

(4) C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960).

(5) (a) M. M. Schwartz and J. E. Leffler, *ibid.*, **90**, 1368 (1968); (b) M. M. Schwartz, Ph.D. Dissertation, Florida State University, 1970.

(6) P. H. Kasai, P. A. Clark, and E. B. Whipple, *J. Amer. Chem. Soc.*, **92**, 2640 (1970).

(7) We are indebted to Drs. James Charlton and Joachim Bargon for their advice and for carrying out some of the CIDNP experiments.

(8) Such a signal would not be easy to detect since it would be generated only during the early stages of the reaction while the background from undecomposed peroxide was still high.

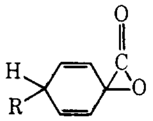
(9) D. B. Denney and G. Feig, *J. Amer. Chem. Soc.*, **81**, 5322 (1959).

(10) (a) L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, **31**, 3821 (1966); (b) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963).

(11) N. A. Milas and A. Golubovic, *ibid.*, **80**, 5994 (1958).

(12) D. F. DeTar, *ibid.*, **89**, 4058 (1967).

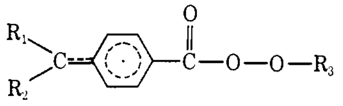
(13) D. H. Hey and J. Peters, *J. Chem. Soc.*, 79 (1960).



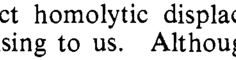
IV

peroxide as a substrate compared with other substituted benzenes seems to require the concerted mechanism or a fast second step that effectively prevents the reversal[14] of the addition of the attacking radical whenever the addition is at an ortho or para position. The fast second step might be either the formation of Walling's lactone or hydrogen transfer. The negligible deuterium isotope effect can be accommodated by Walling's concerted mechanism and by either of the two-step mechanisms if the second step is fast.

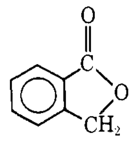
In the present study we have generated the radicals Va–Vf by hydrogen abstraction from the related peroxides. Because they are π radicals they might have been expected to interact with the peroxide functional group *via* the π-electron system, possibly forming an α lactone, VI. On the other hand the intramolecular transfer of a hydrogen atom seems unlikely in the case of the α-cumyl radical substituents and extremely unlikely in the case of the others. In any event, *none of the radicals Va–Vf underwent any measurable loss of the peroxide group.* The peroxide corresponding to Vg decomposed, but to a complicated mixture of products apparently involving extensive cleavage of the ether linkage. The other radicals generated by brominating the corresponding alkyl-substituted peroxide with NBS[15] in CCl_4 were found to undergo extensive conversion to the α-brominated peroxides without decomposition. Similar results were obtained with the meta isomer and even the ortho isomer of Vd. The failure of the ortho isomer to give the five-membered lactone VII by the direct homolytic displacement route was somewhat surprising to us. Although benzyl radicals do not attack benzoyl peroxide in a related intermolecular reaction,[16] a benzhydryl radical substituent is known to cyclize to the lactone VIII.[10b,17,18]



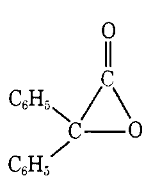
Va, $R_1 = R_2 = H$; $R_3 =$ *tert*-butyl
b, $R_1 = H$; $R_2 = C_6H_5$; $R_3 =$ *tert*-butyl
c, $R_1 = R_2 = CH_3$; $R_3 =$ *tert*-butyl
d, $R_1 = R_2 = H$; $R_3 =$ *p*-methylbenzoyl
e, $R_1 = H$; $R_2 = C_6H_5$; $R_3 =$ *p*-benzylbenzoyl
f, $R_1 = R_2 = CH_3$; $R_3 =$ *p*-isopropylbenzoyl
g, $R_1 = H$; $R_2 = CH_3O$; $R_3 =$ *p*-methoxymethylbenzoyl



VI



VII



VIII

Although our results seem to support the Cadogan mechanism rather than one involving an α-lactone intermediate, they are certainly not conclusive in this regard. First of all, the unpaired electron density calculated for the carbon bearing the acyl peroxide functional group in V is much less than that in III. Secondly, there is the question of radical lifetimes, which becomes important in a nonconcerted variant of the Walling mechanism. Our radicals are scavenged by bromine in a reaction that should be quite fast even though the steady-state concentration of Br_2 in the NBS reaction mixture is low. We note, for example, that it is possible to brominate triphenylmethane with this reagent without decomposing added benzoyl peroxide even though trityl radicals are known to react with the peroxide.[5b]

Experimental Section[19]

All substituted *tert*-butyl perbenzoates were prepared by the method of Bartlett and Hiatt[20a] and were characterized by iodometric titration and by their ir and nmr spectra, features of which are summarized in Table I.

***tert*-Butyl *p*-Benzylperbenzoate.** This perester melted at 56.5–58°.

Anal. Calcd: C, 76.03; H, 7.09. Found: C, 76.28; H, 7.00.

The diacyl peroxides were prepared from the corresponding acid chloride and sodium peroxide or lithium peroxide using procedures patterned after that given in "Organic Syntheses" for the preparation of bis(*p*-nitrobenzoyl) peroxide.[21] They were characterized by melting points, infrared and nmr spectroscopy (Table I), and iodometric titration.

Bis(*p*-bromomethylbenzoyl) Peroxide. A mixture of *p*-bromomethylbenzoyl bromide and *p*-bromomethylbenzoyl chloride was prepared from *p*-toluoyl chloride by the method of Titley.[22] A solution of 3.4 g ($1.22–1.45 \times 10^{-2}$ mol) of this material in 30 ml of 1:1 hexane–ether was added during a period of 50 min to a rapidly stirred cold solution of 0.334 g (7.3×10^{-3} mol) of Li_2O_2 in 20 ml of H_2O in a reaction vessel cooled with an ice bath. After an additional 90-min stirring, the peroxide was dissolved in 100 ml of $CHCl_3$ and 100 ml of CH_2Cl_2 and filtered, the solution was dried over $MgSO_4$, and the peroxide was reprecipitated by adding CH_3OH. The solid product, 0.45 g, melted at 157° dec, 160° dec after recrystallization from CH_2Cl_2 at −20°.

Anal. Calcd: C, 44.89; H, 2.83; Br, 37.33. Found (before recrystallization): C, 44.63; H, 2.67; Br, 36.35. Found (after recrystallization): C, 45.81; H, 2.90; Br, 38.18. The product was too insoluble for nmr, but gave an ir carbonyl doublet in $CDCl_3$ at 1770 (stronger) and 1780 cm^{-1} (weaker).

Bromination of the Peresters. The following procedure, illustrated with *tert*-butyl *p*-methylperbenzoate, was also used for the reaction of the *p*-benzyl- and *p*-isopropylperbenzoates with *N*-bromosuccinimide.

To a 75-ml flask equipped with reflux condenser and $CaSO_4$ drying tube were added 2.08 g (0.01 mol) of *tert*-butyl *p*-methyl-

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[14] The addition of *benzoyloxy* radicals to benzene has recently been shown to be reversible by H. C. Curtis, Ph.D. Dissertation, Florida State University, 1970.

[15] (a) J. C. Martin and R. E. Pearson, *J. Amer. Chem. Soc.*, **85**, 3142 (1963); (b) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); (c) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963).

[16] P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

[17] See also ref 10a and 11 in which neighboring radical groups induce the formation of an α lactone, and ref 18a and 18b in which peroxide homolysis is found to be anchimerically assisted by *o*-iodo and *o*-phenylthiyl.

[18] (a) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Amer. Chem. Soc.*, **80**, 5435 (1958); (b) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

[19] See ref 5b.

[20] (a) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (b) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5226 (1950).

[21] C. C. Price and E. Krebs, "Organic Syntheses," Collect. Vol. 3, Wiley, 1955, p 649.

[22] (a) A. F. Titley, *J. Chem. Soc.*, 2571 (1928). (b) An nmr of the reagent indicated the presence of a small amount of impurity with a Br_2CH side chain.

Table I

Substituent	C=O,[a] cm^{-1}	Nmr[b]
		tert-Butyl Perbenzoates
p-Methyl	1750[c]	δ 7.1–8.1 (m, 4.0, ArH); 2.58 (s, 3.0, CH_3); 1.38 (s, 9.1, $(CH_3)_3C$)
p-Isopropyl	1755	δ 7.8–8.1 (m, 3.8, ArH); 3.00 (m, 1.1, $(CH_3)_2CH$, $J = 7$); 1.38 (s, 9.1, $(CH_3)_3C$); 1.28 (d, 6.0, $(CH_3)_2$-CH, $J = 7$ Hz)
p-Benzyl	1755	δ 7.0–8.0 (m, 9.1, ArH); 3.95 (s, 2.1, CH_2); 1.37 (s, 8.8, $(CH_3)_3C$)
		Benzoyl Peroxides[d]
p-Methyl[h]	(1750,[g] 1770)[e]	δ[f] 7.3–8.3 (m, 4.1, ArH); 2.48 (s, 2.9, CH_3)
m-Methyl[i]	(1760, 1780)	δ 7.2–8.0 (m, 4.0, ArH); 2.41 (s, 3.0, CH_3)
o-Methyl[j]	1760, 1780	δ 6.9–7.8 (m, 4.1, ArH); 2.49 (s, 2.9, CH_3)
p-Isopropyl[k]	1755, 1780	δ 7.16–8.16 (m, 3.8, ArH); 2.95 (m, 0.94, $(CH_3)_2CH$, $J = 7$ Hz); 1.26 (d, 6.3, $(CH_3)_2C$, $J = 7$ Hz)
p-Benzyl[l]	1765, 1780	δ 7.2–8.1 (m, 9.2, ArH); 4.03 (s, 1.8, CH_2)

[a] Carbonyl infrared frequency, in CCl_4 unless otherwise noted. [b] In CCl_4 unless otherwise noted. Shifts (δ) are in parts per million downfield from TMS on a Varian Model A-60 (60 MHz) spectrometer. Data in parentheses are multiplicity, integrated intensity, and assignment. [c] Neat. [d] Symmetrically substituted. [e] In $CHCl_3$. [f] In $CDCl_3$. [g] In each case the stronger band of the doublet is given first. [h] The melting point after crystallization from chloroform–methanol was 135°.[20b] [i] Mp 49–50°, lit.[20b] 54–54.5°. [j] Mp 49–50° [W. Cooper (*J. Chem. Soc.*, 3106 (1951)) reports mp 54°]. [k] Mp 88–89° dec [W. P. Neumann, K. Rubsamen, and R. Sommer (*Chem. Ber.*, **100**, 69 (1967)) report mp 98°]. [l] Mp 89.5–90° dec [F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom (*J. Org. Chem.*, **25**, 1790 (1960)) report mp 87–88°].

perbenzoate, 1.78 g (0.01 mol) of NBS, 0.04 g (2×10^{-4} mol) of benzoyl peroxide, and 26 ml of CCl_4. The ir spectrum of the supernatant liquid was taken in a 0.05-mm CaF_2 cell; no reference cell was used. The nmr spectrum was taken.

The mixture was then refluxed on a steam bath for 105 min and cooled to room temperature. The ir spectrum was retaken and in all cases it was found that the intensity of the C=O band was unchanged and there were no new C=O bands other than that due to succinimide. The solution was then stored overnight at −20° and filtered from succinimide, and its nmr spectrum was taken. Ignoring the negligible contribution from the benzoyl peroxide, the integrated intensities from the aromatic and *tert*-butyl regions of the nmr spectrum were set equal to 13 hydrogens and the relative amounts of the various part structures calculated accordingly (Table II). The methyl esters were used as model compounds to verify the assignments of the brominated side-chain peaks.

Table II. Nmr Spectrum of *tert*-Butyl *p*-Methylperbenzoate after Reaction with NBS in CCl_4

Peak, δ	Assignment	Integrated intensity	Group recovery[a]
7.12–8.18	*p*-Phenylene	50	1.04
6.73	$Br_2\mathit{H}CAr$	2	0.17
4.50	$Br\mathit{H}_2CAr$	16	0.67
2.42	H_3CAr	5.6	0.15
1.37	$(C\mathit{H}_3)_3C$	105.4	0.98
	Total para substituents		0.99

[a] Relative to *p*-phenylene + *tert*-butyl = 13.00 protons.

In the reaction of *tert*-butyl *p*-isopropylperbenzoate with NBS, bromination was shown by the reduction of the nmr $(CH_3)_2CH$ doublet at δ 1.28 almost to the noise level and the appearance of the $(CH_3)_2CBr$ singlet at δ 2.12.[23] The strength of the latter was about 0.8 times that of the *tert*-butyl signal after adjusting for the number of protons in the two groups. In the reaction of *tert*-butyl *p*-benzylperbenzoate the CH_2 singlet at δ 3.95 vanished in the noise level and was replaced by the Ar_2CHBr singlet at δ 6.21. The relative recoveries of the *tert*-butyl, aromatic, and Ar_2CHBr structures as estimated from the integrated intensities were 1.02, 0.98, and 0.7 ± 0.3, respectively.

Bromination of the Dibenzoyl Peroxides. About 5×10^{-4} mol of the substituted peroxide and 5×10^{-4} mol of NBS were dissolved in 5 ml of CH_2Cl_2. An ir spectrum of the solution was taken in a 0.05-mm CaF_2 cell. An aliquot of the solution was concentrated to dryness under vacuum and redissolved in $CDCl_3$, and its nmr spectrum determined.

The reaction mixture was then irradiated with a 300-W Westinghouse reflector tungsten lamp, which also keeps the solution refluxing.[24] The irradiation was continued until a starch–iodide test for NBS was negative (15–45 min, depending on the peroxide). The reaction mixture was then cooled to room temperature and its ir spectrum again recorded. The intensities of the peroxide C=O bands were always within ±2% of their original values except in the case of bis(*p*-methoxymethylbenzoyl) peroxide.

An aliquot was then evaporated to dryness and redissolved in $CDCl_3$ for an nmr spectrum.

In the bromination of bis(*p*-methylbenzoyl) peroxide, the product bis(*p*-bromomethylbenzoyl) peroxide crystallized from the solution as fine needles, mp 161.5° dec. The C=O absorptions of this product in $CHCl_3$ are at 1770 (stronger) and 1780 cm^{-1}. The compound is only very sparingly soluble in $CHCl_3$.

Anal. Calcd for $C_{16}H_{12}O_4Br_2$: C, 44.89; H, 2.83; Br, 37.33. Found: C, 44.78; H, 2.88; Br, 37.40.

The symmetrical structure assigned is based on the analysis, comparison with material synthesized by another route (*vide supra*), and the fact that NBS brominates toluene about five times as fast as it brominates benzyl bromide.[25]

The apparent concentrations of part structures before and after reaction of the various symmetrically substituted dibenzoyl peroxides are given in Table III. These were calculated by assuming no loss of aromatic protons and adjusting the integrated intensities for the other groups according to the number of protons in each structure.

Table III

Dibenzoyl peroxide	Structure and chemical shift, δ in $CDCl_3$		Rel concn of structure	
			Before reaction	After reaction
p-Benzyl	CH_2	4.03	0.83	0.36
	CHBr	6.38	0.00	0.40
p-Isopropyl	$(CH_3)_2CH$	1.26	0.83	0.72
	$(CH_3)_2CBr$	2.23	0.00	0.22
m-Methyl	CH_3	2.41	0.90	0.58
	CH_2Br	4.62	0.00	0.36
o-Methyl	CH_3	2.49	1.1	0.61
	CH_2Br	4.98	0.00	0.34
p-Methyl[a]	CH_3	2.48	1.09	0.54
	CH_2Br	4.58	0.00	0.51

[a] The product was only partially dissolved.

Bis(*p*-methoxymethylbenzoyl) Peroxide. This peroxide was prepared from a hexane solution of the acid chloride and a cold aqueous solution of Li_2O_2 in the usual way. After crystallization

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(23) The $(CH_3)_2CBr$–C_6H_5 signal is at δ 2.12: G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

(24) Control experiments show that the irradiation produces negligible decomposition of the peroxides.

(25) S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **34**, 900 (1969).

from cold $CHCl_3$–CH_3OH it melted at 83.5–84° dec. It was further characterized by its nmr and ir spectra (1770 and 1800 cm^{-1}).

Anal. Calcd: C, 65.44; H, 5.49. Found: C, 65.51; H, 5.47.

The reaction with NBS in $CDCl_3$ decomposed the peroxide extensively to a complex mixture. This was not further investigated after it became clear from the nmr spectrum that extensive degradation of the CH_3O part structure had occurred.[26]

Acknowledgment. This research was supported by the National Science Foundation and in part by PHS Research Grant No. AM 10489 from the Institute of Arthritis and Metabolic Diseases.

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[26] See ref 25 for cleavage of methyl benzyl ether by the same reagent.

Steric Effects of *N*-Alkyl Groups on the First Acid Ionization Constant of 1,10-Phenanthroline

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Earlham College, Richmond, Indiana 47374. *Received June 18, 1970*

Abstract: Acid ionization constants of protonated *N*-methyl- and *N*-ethyl-1,10-phenanthrolinium cations were determined spectrophotometrically in sulfuric acid solutions and compared with ionization constants of diprotonated 1,10-phenanthroline and of analogous bipyridyl cations. Ionization constant ratios $K_{BH_2^{2+}}/K_{BHR^{2+}}$ of 0.28 and 0.039 for R = CH_3 and R = C_2H_5 in the phenanthroline series indicate a steric effect for which a minimum quantitative value is estimated.

A procedure for the quantitative evaluation of the effect of hydrogen bonding on the strengths of dibasic acids was advanced by Westheimer and Benfey[1] and applied to the ionization constants of diprotonated 2,2′-bipyridyl and of its protonated *N*-alkyl cation. In the absence of hydrogen bonding, the ratio $K_{BH_2^{2+}}/K_{BHR^{2+}}$ of the ionization constants of the diprotonated amine and of the corresponding protonated *N*-alkyl cation was assumed to be equal to the statistical factor 2. Hydrogen bonding would stabilize the monoprotonated species BH^+, leading to an increased $K_{BH_2^{2+}}$ value and hence to a larger value for the ratio $K_{BH_2^{2+}}/K_{BHR^{2+}}$. No value less than 2 for this ratio was expected. In the bipyridyl case, $K_{BH_2^{2+}}/K_{BHR^{2+}}$ was found to be 6.7.

It was of interest to consider the corresponding hydrogen-bonding and possible steric effects in 1,10-phenanthroline in which the two pyridine rings are rigidly maintained in the coplanar cis position ideally suited for internal hydrogen bonding of the monoprotonated species.

Experimental Section

All melting points were determined on a Kofler micro hot stage. Spectra were recorded on a Beckman DB spectrophotometer and precise measurements in the 278-mμ region were obtained on a Beckman DU spectrophotometer at 23 ± 2°.

1,10-Phenanthroline. Eastman Organic Chemical's 1,10-phenanthroline monohydrate, dehydrates 97–98°, mp 117 5–119°, was dried *in vacuo* over silica gel for 5 hr.

***N*-Methyl-1,10-phenanthrolinium Iodide.** 1,10-Phenanthroline monohydrate (2.0 g) and methyl iodide (6.8 g) were warmed in nitrobenzene (50 ml) at 37° for 24 hr.[2] Crystals were separated and more methyl iodide (4.6 g) was added to the reaction mixture, which was heated at 37° for a further 24 hr. After washing with benzene, recrystallization to constant melting point from ethanol containing a few drops of water and drying at 107° over P_2O_5 *in vacuo* gave fine yellow plates: mp 200–203°; total yield 1.8 g or 53%. Its ultraviolet spectrum in H_2O shows peaks at 221 (partly due to iodide ion) and 271 mμ (ε 3.2 × 10^4). *Anal.* Calcd for $C_{13}H_{11}N_2I$: C, 48.5; H, 3.44; I, 39.4; N, 8.70. Found: C, 48.3; H, 3.41; I, 39.4; N, 8.76.

***N*-Ethyl-1,10-phenanthrolinium Iodide.** A mixture of 1,10-phenanthroline monohydrate (5.0 g) and ethyl iodide (42 g, bp 71.0–71.3°, uncorrected) in nitrobenzene (100 ml) was heated at 80–95° for 48 hr. After chilling the mixture, yellow needles were separated, washed with benzene, and recrystallized to constant melting point (fine yellow plates) from absolute ethanol: yield 4.4 g or 52%; mp: after drying over silica gel, 184.0–184.5°; after drying at 107° over P_2O_5 *in vacuo*, 180.0–181.5°. Its ultraviolet spectrum in H_2O shows a peak at 221 mμ partly due to iodide ion and a flat peak at 270–273 mμ (ε 3.2 × 10^4). *Anal.* Calcd for $C_{14}H_{13}N_2I$: C, 50.0; H, 3.90; I, 37.8; N, 8.33. Found: C, 49.8; H, 3.99; I, 37.6; N, 8.14.

Preparation of Test Solutions of *N*-Alkyl-1,10-phenanthrolinium Chlorides. The *N*-methyl- and *N*-ethyl-1,10-phenanthrolinium iodides were converted to the corresponding chlorides by shaking with freshly prepared silver chloride according to the method of Westheimer and Benfey.[1] The *N*-methyl cation has peaks at 218 (ε 3.3 × 10^4) and 271 mμ (ε 3.2 × 10^4). The *N*-ethyl cation has a peak at 215 mμ (ε 3.2 × 10^4) and a flat peak at 270–273 mμ (ε 3.2 × 10^4).

Determination of Ionization Constants of 1,10-Phenanthroline and of Its *N*-Methyl and *N*-Ethyl Cations. The spectrophotometric procedure has been described earlier.[1] H_0 values are those of Paul and Long.[3] No significant lateral shifts due to solvent were detected. Spectral data and ionization constant calculations are shown in Table I.

1,10-Phenanthroline. Our value $pK_{BH_2^{2+}} = -1.55 \pm 0.05$ ($K = 35.5$) obtained at 278 mμ compares with $pK_{BH_2^{2+}} = -1.6$ of Linnell and Kaczmarczyk,[4] determined from the variation of molar extinction coefficients at the maximum for each band as H_0 changes.

***N*-Methyl-1,10-phenanthrolinium Cation.** The protonated *N*-methyl cation has maxima at 225 (ε 2.9 × 10^4) and 278 mμ (ε 4.1 × 10^4). Extinction coefficients at 278 mμ at varying values of H_0 yielded $pK_{BHR^{2+}} = -2.11 \pm 0.09$ ($K = 129$).

***N*-Ethyl-1,10-phenanthrolinium Cation.** The protonated *N*-ethyl cation has maxima at 226 (ε 2.4 × 10^4) and 279 mμ (ε 3.8 × 10^4).

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