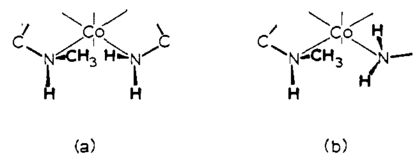

Figure 3. Regions of the *trans,trans*-[Co(Meen)$_2$X$_2$]$^+$ isomers exhibiting steric compression: (a) *meso* isomer; (b) *d,l* isomer.

conformation, the steric compression is most pronounced and the signal of the H$_a$ proton appears at a lower field than that in the other diastereomer. If the methyl group occupies position H$_a$, as in the DD-EDDP compound, the position of the methyl group signal in the complex with the k′ conformation is at a lower field than the other diastereomer.

Table II. Nmr Data for *trans*-(O)-[Co(en)(EDDA)]$^+$-Type Complexes^{a,b}

Complex	H$_a$	H$_b$	CH$_3$^{f}	Ref
[Co(en)(EDDA)]$^+$	4.19	3.37		4
[Co(*l*-pn)(EDDA)]$^{+\ c}$	4.26 4.23	3.36		4
[Co(*d*-pn)(EDDA)]$^{+\ d,e}$	4.16	3.34		4
[Co(en)(LL-EDDP)]$^+$	3.99		1.45	3
[Co(*l*-pn)(LL-EDDP)]$^{+\ c}$	4.15 4.08		1.45	3
[Co(*d*-pn)(LL-EDDP)]$^{+\ d,e}$	3.93		1.47	3
[Co(en)(DD-EDDP)]$^+$		3.53	1.55	3
[Co(*l*-pn)(DD-EDDP)]$^{+\ c}$		3.54	1.61	3
[Co(*d*-pn)(DD-EDDP)]$^{+\ d,e}$		3.51	1.53	

^{a} Complexes with Λ(C$_8$) absolute configuration. ^{b} Shifts in ppm from DSS. ^{c} k′ diamine conformation. ^{d} k diamine conformation. ^{e} Signal from enantiomeric compound. ^{f} Methyl signal from EDDP.

The technique is also useful for a series of *trans*-bis(diamine)cobalt(III) complexes. Buckingham, Marzilli, and Sargeson[17] have prepared the *meso*- and *d,l*-*trans,trans*-[Co(N-Meen)$_2$X$_2$]$^+$ compounds where X is NO$_2^-$, Cl$^-$ or $^1/_2$NO$_2^-$, $^1/_2$Cl$^-$. Corey and Bailar[15] have discussed the different interactions between the possible conformations for the diamine rings. They concluded that the most stable situation exists when both rings have the same conformation (kk or k′k′) as found in the *d,l* isomers (Figure 3b). The *meso* isomer (Figure 3a) has one ring as k and one as k′, which should be less stable than the racemate because of the interaction in the *meso* isomer between the methyl group attached to one nitrogen atom and the proton on the neighboring nitrogen. The nmr data of these compounds show that this methyl group is involved in a compression when compared with the racemate (Table III).

Table III. Nmr Spectra of *trans,trans*-[Co(N-Meen)$_2$X$_2$]$^{+\ a,b}$

X$_2$	*meso*^{c}	*d,l*^{c}
NO$_2^-$	2.34	2.23
$^1/_2$NO$_2^-$, $^1/_2$Cl$^-$	2.4 2.57	2.29 2.46
Cl$^-$	2.4	2.37

^{a} Shift in ppm from DSS. ^{b} N-Meen = N-methylethylenediamine. ^{c} Methyl group signal.

Acknowledgment. The financial support of the National Institute of Health (Grant AM-12262) in this research is gratefully appreciated. The cooperation of Dr. William Kreuger of the Upjohn Company, Kalamazoo, Mich., in allowing the use of a Cary 60 for recording CD measurements is also appreciated.

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Received October 2, 1969

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Transient Bromine Atom Charge-Transfer Complexes Observed by Pulse Radiolysis[1]

Sir:

Pulse radiolysis[2] has been used to study transient charge-transfer complexes in organic reactions. It is known from kinetic spectroscopy data[3-6] that iodine and chlorine atoms can form complexes with various electron donors. Only little is known about bromine atom complexes.[7] Bromobenzene as well as various liquid systems with aliphatic and aromatic bromine compounds were studied at room temperature. In all

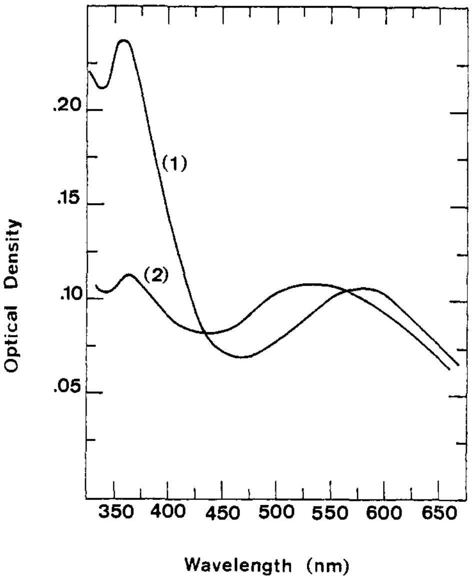

Figure 1. Transient absorption spectra at the end of an electron pulse: (1) in pure deaerated bromobenzene; (2) in oxygen-saturated bromobenzene.

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(1) Work supported in part by the Swiss National Funds. Publication II of a series on Pulse Radiolysis of Organic Halogen Compounds.

(2) Pulse radiolysis apparatus by J. P. Keene, *J. Sci. Instrum.*, **41**, 493 (1964): 4-MeV LINAC, 2-μsec pulse width, 0.4-μsec time resolution; standard dose, 4 × 10^{17} eV/g.

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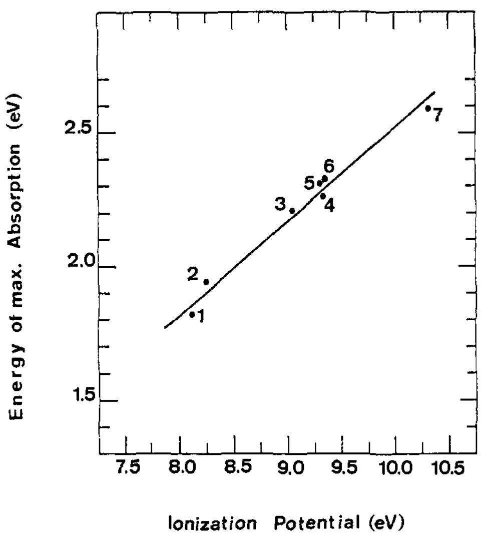

Figure 2. Plot of $h\nu_{max}$ *vs.* ionization potential for Br atom charge-transfer complexes: (1) naphthalene (0.3 *M*) in bromoform (λ_{max} 680 nm); (2) diphenyl (0.3 *M*) in bromoform (λ_{max} 640 nm); (3) pure bromobenzene (λ_{max} 560 nm); (4) CBr_4 (0.92 *M*) in benzene (λ_{max} 550 nm); (5) $CHBr_3$ (2 *M*) in benzene (λ_{max} 540 nm); (6) CCl_3Br (2 *M*) in benzene (λ_{max} 535 nm); (7) pure bromocyclohexane (λ_{max} 480 nm; ionization potential in analogy to other bromohydrocarbons).

systems short-lived bromine atom charge-transfer complexes were detected.

Two absorption bands are formed in pure deaerated liquid bromobenzene: an intense short-lived absorption ($\tau_{1/2}$ = 90 μsec) in the near-ultraviolet (λ_{max} 355 nm), previously described by MacLachlan and McCarthy,[8] and a very broad, less intense and fast decaying visible band centered at 560 nm (Figure 1). The latter we assign to the charge-transfer complex of the bromine atom with bromobenzene ($Br \leftarrow BrC_6H_5$). A test for charge-transfer complexes[4,6,9] in the system investigated is shown in Figure 2, in which the energy of the absorption maximum of the observed visible band is plotted against the ionization potential of the electron donor. Such a linear relationship is discussed by Briegleb[9] and by Mulliken and Person.[10] It is used here as proof for our complex assignment.

The visible band cannot be due to ions or excited states for the following reasons. (1) The *G* values of free ions (number of particles produced per 100 eV of absorbed energy) in similar solvents[11,12] do not allow the yield of ions in bromobenzene to be greater than *G* (ion pairs) ≈ 0.15, this being much lower than the estimated yield of complex (see below). (2) Charge scavenging with triphenylmethane[13] (10^{-2} *M*) does not yield measurable triphenylcarbonium ions ($G_{TPC+} < 0.04$). (3) Singlet excited states are too short-lived[14] for our technique. (4) Oxygen should quench the visible band if it were the triplet state of bromobenzene in contrast to Figure 2. There are indications that the triplet absorption is within the 355-nm band.[8] (5) Flash photolysis of pure bromobenzene did not yield a transient absorption in the visible, whereas selective flash photolysis of Br_2 (2×10^{-3} *M*) dissolved in bromobenzene produced the same band at 560 nm.

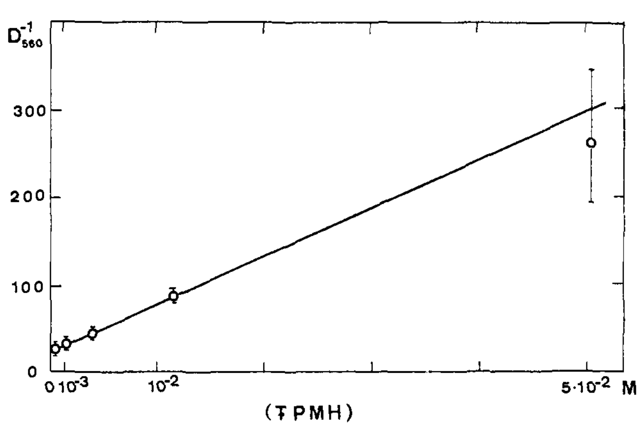

Figure 3. (Optical density at 560 nm)$^{-1}$ *vs.* TMPH concentration.

The extinction coefficient of the bromine atom complex with bromobenzene at 560 nm was estimated by competing for bromine atoms by triphenylmethane in bromobenzene solutions. The following reactions occur.

$$Br + BrC_6H_5 \xrightarrow{k_1} (Br \leftarrow BrC_6H_5)$$

$$Br + TPMH \xrightarrow{k_2} TPM\cdot + HBr$$

A simple linear relationship between the reciprocal *G* value of complex formation and the triphenylmethane (TPMH) concentration is predicted if no interfering reactions occur.

$$\frac{1}{G_{complex}} = \frac{1}{G_{Br}} + \frac{k_2(TPMH)}{k_1(BrC_6H_5)G_{Br}}$$

The results are given in Figure 3. On the basis of the above reactions and from the changes of the absorptions at 560 (complex only) and 510 nm (TPM radical and complex), the extinction coefficient of the complex can be calculated using $\epsilon(TPM\cdot)_{510\ nm} = 632\ M^{-1}\ cm^{-1}$. The extinction coefficient of $Br \leftarrow BrC_6H_5$ was found to be $\epsilon_{560} = 2800 \pm 500\ M^{-1}\ cm^{-1}$. The corresponding yield becomes *G*(complex) = 1.8 ± 0.3.

The decay of the complex in pure deaerated bromobenzene is exponential with time over three half-lives. The slope of the logarithmic plot is, however, dose dependent. For 5500 rads the apparent rate constant is $k_1 = 0.34 \pm 0.04 \times 10^6\ sec^{-1}$ and is constant over the full range of the visible spectrum (520–660 nm). This shows that the absorption band is due to a single transient species. The buildup reaction is faster than the response time of our apparatus. We therefore cannot decide whether the complex is formed by radical–molecule reaction or by ionic recombination.[15,16]

In oxygen-saturated solutions of bromobenzene the absorption at 560 nm on pulsing broadens toward shorter wavelengths (Figure 1). It was shown by flash photolysis as well as by chemical synthesis that the addi-

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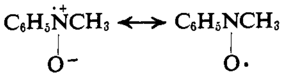
Received October 30, 1969

Proton Magnetic Resonance Emission in the Intramolecular Rearrangement of a Tertiary Amine Oxide

Sir:

Several recent studies[1–3] present evidence for a radical nitrogen to oxygen group migration in the thermal Meisenheimer rearrangement[4] of amine oxides. At temperatures 40° below that required for a significant rate of rearrangement, steady-state N-methyl-N-phenylnitroxyl radical (I) concentrations were clearly charac-



$$C_6H_5\overset{+}{\underset{|}{N}}CH_3 \longleftrightarrow C_6H_5\underset{|}{N}CH_3$$
$$\qquad O^- \qquad\qquad\qquad O\cdot$$

I

terized by esr measurements on solutions of N-methyl-N-benzylaniline oxide.[1] I may not actually participate in the rearrangement since very slow O-substituted product formation occurs under these conditions and no benzyl radicals were detected. However, under rearrangement conditions the effect of *para* substituents in either the benzyl[1] or phenyl[2] rings is very small ($\rho \sim 0.9$), as would be expected in a radical process. Oxygen trapping even at high pressure reduced the product by only two-thirds.[3] Thus a nonradical route[4] or a caged radical pair[3] has been postulated to account for the untrapped rearrangement product. Evidence for radical pair participation in rearrangement processes can also be obtained by proton magnetic resonance (pmr) emission and enhanced absorption in reaction products.[5] We have now used pmr emission to obtain direct evidence for both nitroxyl and benzyl radicals in the rearrangement of a tertiary amine oxide.

The pmr spectrum of N,N-dimethylbenzylamine oxide (II)[6] was scanned during thermal rearrangement at 130–155°.[8] In the region δ 2.0–5.2 ppm (Figure 1), emission singlets were observed at δ 2.5 and 4.6 ppm.[9] These signals, from the methyl and methylene protons, respectively, in the rearrangement product N,N-dimethyl-O-benzylhydroxylamine (III) are respectively upfield and downfield from the comparable singlets of II. Aqueous solutions from vacuum concentration of the amine oxide preparation after destruction of hydrogen peroxide have generally been used[7,10,11] in producing III by thermolysis of II. A pmr scan, started 3.9 min after placing such a solution in the preheated (148°) probe, had a strong water peak centered at 4.0 ppm (Figure 1a). This solution had measurable emission for more than 50 min. Since preparative rearrangement is carried out at elevated temperatures (85–165°[7,10,11]) under vacuum, water evaporates rapidly during this reaction. Pmr measurements under these conditions were not viable; therefore we sought to remove all water by freeze drying the material at 0.01 Torr. The hygroscopic free flowing white powder, mp 63–66°, obtained in this fashion was found (pmr in $CDCl_3$) to be a monohydrate with a bound water peak at 5.03 ppm. When the neat solid is heated to 130°, the water peak gradually shifts from slightly

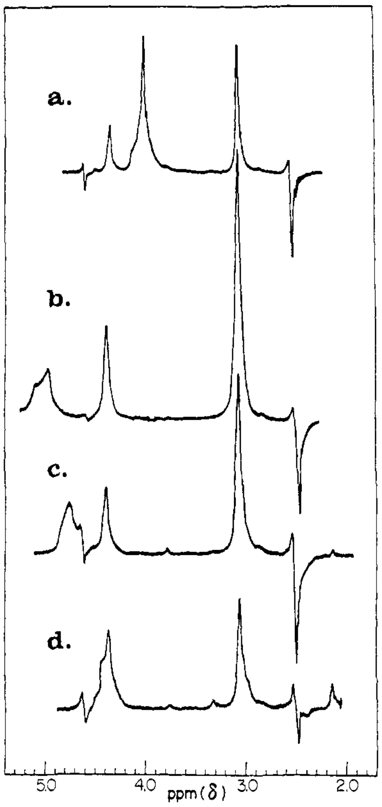


Figure 1. Proton magnetic resonance spectra of the emission-active region in the N,N-dimethylbenzylamine oxide (II) layer (lower phase of two phase system) during thermal conversion to N,N-dimethyl-O-benzylhydroxylamine (III): (a) scan started 3.9 min after placing a concentrated aqueous solution of II in the probe at 148°; (b–d) scans started 0.4, 4.5, and 10.0 min after placing the crystalline monohydrate of II in the probe at 130°.

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[9] Peak shifts of −0.07 and −0.05 ppm, respectively, were noted when the moisture content of the sample was minimized. All peaks are assigned relative to the 3.06 ppm methyl singlet of II as measured at 26° as a 20% solution in $CDCl_3$ with 1% $(CH_3)_4Si$.

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