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References and Notes

(1) R. Scholder and U. Voelskow, *Z. Anorg. Allg. Chem.*, **266**, 256 (1951).
(2) J. S. Magee and R. H. Wood, *Can. J. Chem.*, **43**, 1234 (1965).
(3) D. Meyerstein, *Inorg. Chem.*, **10**, 638, 2244 (1971).
(4) D. C. Olson and J. Vasilekskis, *Inorg. Chem.*, **10**, 463 (1971).
(5) A. Levitzki, M. Anbar, and A. Berger, *Biochemistry*, **6**, 3757 (1967).
(6) A. Levitzki and A. Berger, *Biochemistry*, **10**, 64 (1971).
(7) J. J. Bour and J. J. Steggerda, *Chem. Commun.*, 85 (1967).
(8) J. J. Bour, P. J. M. W. L. Birker, and J. J. Steggerda, *Inorg. Chem.*, **10**, 1202 (1971).
(9) G. L. Burce, E. B. Paniago, and D. W. Margerum, *J. Chem. Soc., Chem. Commun.*, 261 (1975).
(10) G. L. Burce, Ph.D. Thesis, Purdue University, 1975.
(11) G. Shmuckler, *Talanta*, **12**, 281 (1965).
(12) A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).
(13) A. Kaneda and A. E. Martell, *J. Coord. Chem.*, **4**, 137 (1975).
(14) W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, Englewood Cliffs, N.J., 1952, p 217.
(15) F. P. Dwyer, H. A. McKenzie, and R. S. Nyholm, *Proc. R. Soc. N.S. Wales*, **81**, 216 (1947).
(16) P. George, G. I. H. Hanna, and D. H. Irvine, *J. Chem. Soc.*, 3048 (1957).
(17) V. I. Kravtsov and G. M. Petrova, *Russ. J. Inorg. Chem.*, **9**, 552 (1964).
(18) E. Jackson and D. A. Pantony, *J. Appl. Electrochem.*, **1**, 113 (1971).
(19) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935).
(20) G. A. Hamilton, R. D. Libby, and C. R. Hartzell, *Biochem. Biophys. Res. Commun.*, **55**, 333 (1973).

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Low Temperature Photochemical Studies on Acetyl Benzoyl Peroxide. The Observation of Methyl and Phenyl Radicals by Matrix Isolation Infrared Spectroscopy

Sir:

Attempts to photochemically produce radicals in rare gas matrices are usually frustrated by their tendency to recombine. This severely limits the spectroscopic techniques that can be used to detect the presence of a radical. In particular, relatively large concentrations of radicals are required for a reliable infrared identification. Here we report on matrix isolation studies which are capable of producing large concentrations of radicals. The method is related to that used by Box,[1] and Karch and McBride[2] in their elegant EPR and ENDOR studies. These authors generated radical pairs by photoelimination of a small stable molecule from a suitable precursor.

As an initial system, we have chosen diacyl peroxides which when irradiated with ultraviolet light cleave into radical pairs and carbon dioxide. The latter isolates the two simultaneously generated radicals from one another and suppresses their recombination. Warming the argon matrix from liquid helium temperatures to approximately 30 K is expected to "soften" the environment enough to remove the obstruction created by the CO_2 molecules thus allowing the radicals to recombine and act as their own trapping reagents.

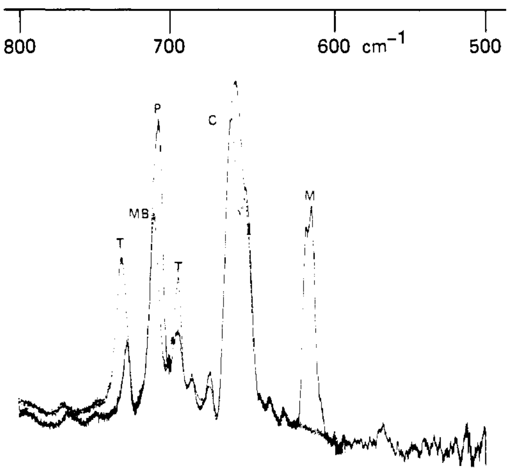


Figure 1. (a) The infrared spectrum of acetyl benzoyl peroxide after extensive irradiation with light longer than 3000 Å (—). (b) The infrared spectrum after warm-up to 30 K (- - -): legend, MB = methyl benzoate, C = carbon dioxide, M = methyl radical, P = phenyl radical.

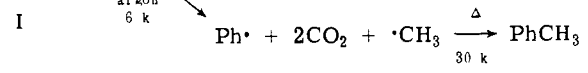
Table I. Fundamental Vibrational Frequencies of the Methyl Radical[a]

		ν_2	ν_3	ν_4
CH_3	*b*	611		
	c	617	1396	3162
	d	612	1385	3150
CD_3	*b*	463		
	c	463	1026	2381
	d	461	1029	2369

[a] ν_2 = out of plane bend, ν_3 = asymmetric in plane bend, ν_4 = asymmetric CH stretch. [b] Reference 9. Produced by the vacuum uv photolysis of methane. Spectra obtained in an argon matrix. [c] Reference 6. Pyrolysis of CH_3I, CD_3I, and $(CH_3)_2Hg$ in neon gas. Spectra obtained in a neon matrix. [d] Present study. Photolysis of $C_6H_5CO_2O_2CCH_3$, $C_6H_5CO_2O_2CCD_3$, and $C_6D_5CO_2O_2CCH_3$ in an argon matrix.

Acetyl benzoyl peroxide (I) was isolated in an argon matrix at 6 K and subsequently irradiated with a medium pressure mercury lamp in conjunction with a 10-cm water filter and a Corning No. 053 UV filter with no transmission below 2900 Å.[3] During the irradiation bands due to CO_2, methyl benzoate,[4] two very intense bands at 710, 612 cm^{-1} and weaker absorptions at 3150, 1385 cm^{-1} appeared. Upon warming the matrix to 30 K all of the bands produced during the irradiation (except those due to CO_2 and methyl benzoate) disappeared after several seconds with the simultaneous appearance of bands due to toluene.[4,5] These results are shown in Figure 1. In Table I literature values of matrix isolation experiments on the methyl radical are given for comparison. From these it follows that the absorptions observed in our experiments at 612, 1385, and 3150 cm^{-1} agree in band center and intensity assignment with the methyl radical. In support of the above claim the matrix photolysis experiments of I with deuterium substitution on the acetyl group produced bands at 461, 1029, and 2369 cm^{-1} due to CD_3 in complete accord with the independent studies of Snelson.[6] Thus, our results and Snelson's firmly establish the ground state vibrational spectrum of the methyl radical. Since it is known[2] that the irradiation of I yields methyl and phenyl radicals simultaneously and since we observe that upon warming the sample to 30 K methyl combines with an other species to produce toluene, we conclude that the intense band at 710 cm^{-1} which disappears synchronously with those assigned to the methyl radical is due to the phenyl radical.[7] We assign the 710-cm^{-1} band of the phenyl radical to a CH out of plane bending mode which are characteristically very intense in the infrared. Scheme I

Scheme I



shows the decomposition mechanism of acetyl benzoyl peroxide.

To our knowledge this is the first infrared detection of the phenyl radical.[8]

In addition, we have also irradiated I with deuterium substitution in the phenyl ring. Photolysis of this species produced the intense 612 cm^{-1} band characteristic of the out of plane bending mode of the methyl radical, the weak 1385, 3150 cm^{-1} bands, and another intense band at 519 cm^{-1} which synchronously disappeared with CH_3 upon warming to 30 K. This intense band at 519 cm^{-1} we assign to the CD out of plane bending mode of the phenyl radical.

Further experimental and theoretical work is being pursued on this system and a more complete account is forthcoming.

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References and Notes

(1) H. C. Box, *J. Phys. Chem.*, **75,** 3426 (1971).
(2) N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Am. Chem Soc.*, in press.
(3) Photolysis was also performed with a filter which transmitted between 3000 and 4000 Å. These conditions did not change any observations.
(4) Species identified by comparison with the matrix ir spectrum of an authentic sample.
(5) Evidence that the integrity of the matrix isolation was maintained during warm up and that the photochemical and thermal reactions occurred within an argon cavity was given by the absence of ethane[4] or diphenyl[4] during the course of the experiments.
(6) A. Snelson, *J. Phys. Chem.*, **74,** 537 (1970).
(7) The possibility of the observed bands stemming from benzoyloxy radicals was excluded on the basis that no carboxyl bands above 1500 cm^{-1} were observed other than those belonging to methyl benzoate. Also warm up experiments did not show an increase in methyl benzoate, the expected combination product of the benzoyloxy–methyl radical pair. In addition, Karch et al.[2] have shown that the benzoyloxy radical is quite photosensitive under similar photolytic conditions to ours. Since their results were obtained using sensitive ESR techniques, we do not expect to see such small concentrations with our relatively insensitive infrared techniques.
(8) For ESR and uv studies on the phenyl radical see P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Am. Chem. Soc.*, **91,** 4364 (1969); J. E. Bennett, B. Mile, and A. Thomas, *Proc. R. Soc., Ser. A*, **293,** 246 (1966); G. Porter and Ward, *ibid.*, **287,** 457 (1965).
(9) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47,** 5146 (1967).

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The Influence of Remote Substituents on Redox Potentials in Nitrosoarene Complexes of Ruthenium

Sir:

The effect of coordinated ligands on the properties of a metal center is a fundamental theme of transition metal chemistry.[1-3] Changes in ligands can lead to changes in the electronic structure of complexes and, with widely varying ligands, the properties of the metal center can be strongly affected. A related question, arising from the study of substituent effects in physical organic chemistry[4,5] and still largely unexplored,[6] concerns the sensitivity of the metal center to changes at a remote site on a ligand. We have prepared the series of *para*-nitrosoarene complexes of ruthenium(II), [*cis*-$Ru(bpy)_2(p\text{-}(N(O)C_6H_4X)Cl]^+$ (bpy is 2,2′-bipyridine; X is $N(CH_3)_2$, $NHCH_3$, OH, Br, H, CH_3, NO_2), and find evidence that even changes in the remote substituent -X can have a profound effect at the metal.

The preparation of the complexes has been described.[7] From spectral studies and the crystal structure of a related palladium complex,[8] it is probable that the ArNO ligands are N-bound. The ruthenium complexes undergo reversible one-electron oxidations and reductions in acetonitrile[9] and have intense absorption bands which can be assigned to dπ → π* (ArNO) and dπ → π* (bpy) transitions. The oxidation processes are electrochemically reversible (eq 1).[9] Their potentials fall in a potential range (Table I) common to related bis(2,2′-bipyridine)ruthenium(III)/(II) couples,[10] and the one-electron oxidation products, $[Ru(bpy)_2(N(O)C_6H_4X)Cl]^{2+}$ (X = $N(CH_3)_2$, $NHCH_3$, H, CH_3), prepared by Ce(IV) oxidation have electronic spectral properties in solution expected for Ru(III).[11,12]

Table I. $E_{1/2}$ Values for the Nitrosoarene Complexes $[Ru(bpy)_2(p\text{-}N(O)C_6H_4X)Cl]^+$ in Acetonitrile[a]

–X	$E_{1/2}$ (OX), V	$E_{1/2}$ (Red), V
$-N(CH_3)_2$	0.77	–0.91
$-NHCH_3$	0.80	–0.90
–OH	0.90	–0.61
$-CH_3$	1.25	–0.71
–H	1.30	–0.69
–Br	1.30	–0.61
$-NO_2$	1.43	–0.39

[a] In 0.1 *M* $[N(n\text{-}C_4H_9)_4]PF_6$–acetonitrile vs. the saturated sodium chloride calomel electrode at 22 + 2° using a Pt bead electrode.

$$[Ru^{III}(bpy)_2(N(O)C_6H_4X)Cl]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}(bpy)_2(N(O)C_6H_4X)Cl]^+ \quad (1)$$

$$E_{1/2}(OX)$$

The reduction processes are reversible only at relatively fast cyclic voltammetry scan rates, occur in the potential range −0.39 to −0.91 V vs. the SSCE (Table I), and are in the correct potential region to be reductions at bound nitrosoarene (eq 2).[13-15]

$$[Ru^{II}(bpy)_2(N(O)C_6H_4X)Cl]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}(bpy)_2(N(O)C_6H_4X\cdot^-)Cl] \quad (2)$$

The increase in Ru(III)/(II) reduction potentials as saturated ligands are replaced by π-accepting ligands is well documented and has been attributed to stabilization of the Ru(II) state by π-back-bonding.[3,16] Monotonic increases from 0.1 to 1.25 V[3,17] are observed for Ru(III)/(II) reduction potentials in acidic aqueous solution in couples from $Ru(NH_3)_3{}^{3+/2+}$ to $Ru(bpy)_3{}^{3+/2+}$ in which NH_3 groups are replaced stepwise by π-back-bonding pyridine ligands. By comparison, the data in Table I are remarkable in that changing the *remote* substituent on the *single* nitrosoarene ligand from $-N(CH_3)_2$ to $-NO_2$ causes an increase in Ru(III)/Ru(II) potential nearly 60% as great (0.77–1.43 V).

The high sensitivity of the filled dπ levels to changes in -X is also reflected in $\bar{\nu}_{max}$ values for the dπ(Ru(II)) → π* (bpy) transitions.[18] For these transitions, which involve the 2,2′-bipyridine groups as "spectator" ligands for the Ru-nitrosoarene interaction, $\bar{\nu}_{max}$ varies directly with $E_{1/2}(OX)$ (Table I) in the range 20.7 kK (X = $N(CH_3)_2$) to 24.1 kK (X = NO_2).

The sensitivity of $E_{1/2}(OX)$ to -X is shown in the Hammett-type plots in Figures 1 and 2. The correlations between $E_{1/2}(OX)$ and the substituent constants σ_R, $\sigma_R{}^0$, and $\sigma_p - \sigma_m$, which have been taken as a measure of pure resonance (π-bonding) effects, are good to excellent.[5,19] The correlation coefficient (r) for the data in Figure 1 is 0.970. The correlation with σ_p (Figure 2) is less satisfactory (r = 0.937). For the plot in Figure 1, the sensitivity of $E_{1/2}(OX)$ to -X is extraordinarily high since the "reaction constant" ρ is 1.05. Much lower reaction constants are observed for redox processes of benzenoid compounds where the substit-