sponding to IX and X. Treatment of this mixture with excess base gave II, while alcoholic hydrogen chloride furnished the indole III. The originally puzzling results discussed in the first paragraph can now be explained by the rapid formation (confirmed by thin layer chromatography) of the enolate anion corresponding to IX, *via* benzoyl and proton transfer. In the absence of additional sodium methoxide, this anion remains in the mixture until work-up, acidification then producing III. With excess base, however, irreversible ring closure to oxindole occurs *via* the dianion of the enol. The mechanism will be discussed more thoroughly in the full paper.

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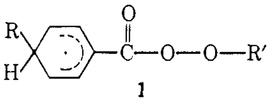
Behavior of a σ Radical with a Peroxide Functional Group

Sir:

Radical-substituted peroxides are of interest in connection with the problem of radical-induced decomposition of peroxides. Attack of radicals on the ring of an aroyl peroxide can give rise to species **1**, **2**, or **3**. Species **1** and/or **2** are believed to be intermediates for induced decomposition.[1] Our results indicate that species **3** does *not* lead to induced decomposition.



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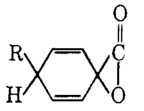

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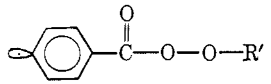
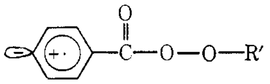


3

Experiment[2,3] and simple molecular orbital considerations agree that the unpaired electron in the ground state of phenyl radicals occupies a carbon sp^2 σ orbital, with very little unpaired spin density in the π system. The isomerization of **3** to structures such as **4**–**6** might require a considerable activation energy, although no accurate theoretical prediction can be made at this time.



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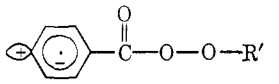

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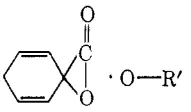

6

We have generated **3** (R′ = *p*-iodobenzoyl) by decomposing bis(*p*-iodobenzoyl) peroxide[4] in degassed carbon tetrachloride at 79.8°. The disappearance of peroxide titer is precisely first order, with $k = 1.84 \times 10^{-5}$ ($\pm 4\%$) sec^{-1}. The products are *p*-diiodobenzene, *p*-dichlorobenzene, *p*-chloroiodobenzene, carbon dioxide, and hexachloroethane, accounting for 100% of the peroxide and excluding the possibility of a first-order, induced-decomposition process.[5] Within experimental error, the yields of *p*-diiodo- and *p*-dichlorobenzenes are equivalent, but are dependent on the initial concentration of peroxide, as shown in Table I.

Table I. Aromatic Products of Decomposition of Bis(*p*-iodobenzoyl) Peroxide in Carbon Tetrachloride

Initial concn of Peroxide, $M \times 10^2$	Moles/mole of peroxide *p*-IPhI	 *p*-ClPhCl	 *p*-ClPhI
1.59	0.14	0.15	1.70
8.02	0.50	0.41	1.21

p-Diiodobenzene can come from *p*-iodophenyl radical attack either on the peroxide itself (leading to **3**) or on *p*-chloroiodobenzene.[6,7] However, upon work-up of the peroxide after about 15% decomposition[8] the *p*-iodo substituents *in the undecomposed peroxide* were found to have been replaced by *p*-chloro substituents to an extent equivalent to ~42% of the peroxide decomposed. It should be noted that the substituent effects of *p*-chloro and *p*-iodo on the unimolecular decomposition of benzoyl peroxide are expected to be indistinguishable.[4,5]

We conclude, therefore, that the *para*-σ radical substituted peroxide is formed without concerted decomposition of the peroxide, and that it persists unchanged long enough to abstract chlorine from solvent, about 10^{-6} to 10^{-7} sec.[9]

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(1) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, 82, 1738 (1960); C. Walling, Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, No. 131; C. Walling and Z. Čekovič, *J. Am. Chem. Soc.*, **89**, 6681 (1967).

(2) G. Porter and B. Ward, *Proc. Roy. Soc.* (London), **A287**, 457 (1965).

(3) J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965).

(4) W. Cooper, *J. Chem. Soc.*, 3106 (1951).

(5) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(6) J. F. Bunnett and C. C. Wamser, *ibid.*, **88**, 5534 (1966).

(7) D. L. Brydon and J. I. G. Cadogan, *Chem. Commun.*, 744 (1966).

(8) Reduction of the undecomposed peroxide with NaI–acetone, followed by acidification, yielded the acids. Treatment of the acids with diazomethane–ether yielded methyl esters, which were separated by vapor phase chromatography.

(9) W. H. Starnes, Jr., *J. Org. Chem.*, **31**, 1436 (1966).

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Catalysis of Ionic Reactions by Polyelectrolytes. Reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} in Polysulfonic Acid Solutions[1]

Sir:

In previous communications from this laboratory[2–4] it was suggested that a polyion should catalyze strongly any reaction involving two counterions. Furthermore, this catalytic effect could be used to study the distribu-

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(2) H. Morawetz and E. W. Westhead, Jr., *J. Polymer Sci.*, **16**, 273 (1955).

(3) H. Morawetz, *ibid.*, **42**, 125 (1960).

(4) H. Morawetz and J. A. Shafer, *J. Phys. Chem.*, **67**, 1293 (1963).

tion of electrostatic potential, provided the spatial distribution of the reactive species is governed solely by long-range electrostatic forces. To date, the predicted catalytic effect has been observed only for reactions of bulky organic reagents,[5-9] and it has been demonstrated that, at least in some of these cases, hydrophobic bonding plays an important role in the interation of the reagent and the polyions.[8,9] We have therefore chosen to investigate the effect of two polyanions (polyvinylsulfonate (PVS) and polymethacryloxyethylsulfonate (PMES)) on the Hg^{2+}-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$. This reaction has been studied extensively in the past in investigations of the kinetic salt effect, and it has the advantage that it may be followed by ultraviolet spectroscopy at extremely high dilution of the reagents. The nature of the reaction in the presence of polyelectrolyte was confirmed by (a) the absence of any spectral change of the cobalt complex over the time scale of the experiments reported in the absence of Hg^{2+} and (b) the identity of the ultraviolet spectrum observed at the end of the reaction with that obtained on addition of $Co(NH_3)_5 \cdot H_2O^{3+}$ to a solution containing the polymeric acid and Hg^{2+}.

The reactions were run at $5 \pm 0.05°$ in solutions adjusted to pH 3 by perchloric acid, containing 5×10^{-6} *M* $Co(NH_3)_5Cl^{2+}$ and 5×10^{-5} *M* Hg^{2+}. Under these conditions, the disappearance of $Co(NH_3)_5Cl^{2+}$ is characterized by a pseudo-first-order rate constant of 2.38×10^{-7} sec^{-1} in the absence of polyelectrolyte. As expected, the catalytic effects produced by the two polyanions were enormous; in the absence of added simple electrolyte and with a polyanion concentration of 5×10^{-5} *N*, the reaction was accelerated by factors of 24,700 with PMES and 176,000 with PVS. The closer proximity of the fixed charges to the backbone of PVS accounts probably for its higher catalytic efficiency.

Addition of simple salts reduces the effect of the polyion on the reaction rate, since increasing counterion concentrations shield the fixed charges of the polyion and reduce its interaction with Hg^{2+} and $Co(NH_3)_5Cl^{2+}$. For instance, in the presence of 0.01, 0.03, and 0.05 *M* $NaClO_4$, the acceleration factors due to PVS fall off to 58,200, 13,000, and 4000.

Table I lists acceleration factors observed in the presence of 0.01 *M* $NaClO_4$. The data show that as the polyion concentration is increased, the reaction rate first increases, but then decreases sharply. This may be explained as follows. As long as the sum of the concentrations of the reagent ion is in large excess over the ionized sites of the polymer, only a small fraction of the reagent ions is held in the polyion domains and the distribution of the counterions in any one of these domains may be considered to be independent of the polyion concentration. The increase of the catalytic effect on polyion addition in the dilute concentration range reflects then the increasing fraction of bound $Co(NH_3)_5Cl^{2+}$. However, in more concentrated polymer solution the binding of both reagents is essentially complete, and further polymer addition distributes the reagents over more polymer domains, reducing the probability of their mutual collision.

Table I. Acceleration of the Hg^{2+}-Catalyzed Aquation of $Co(NH_3)_5Cl^{2+}$ by Polyanions[a]

	Acceleration factor	
Polyanion, *N*	PVS	PMES
1.5×10^{-5}	16,600	2,600
5×10^{-5}	58,200	5,300
1.5×10^{-4}	64,500	11,400
5×10^{-4}	44,100	9,300
1.5×10^{-3}	18,800	3,100

[a] 5×10^{-6} *M* $Co(NH_3)_5Cl^{2+}$, 5×10^{-5} *M* Hg^{2+}, 10^{-2} *M* $NaClO_4$, 5°.

A similar phenomenon is observed if the polyanion concentration is fixed and the Hg^{2+} concentration is varied. As long as only a fraction of the anionic sites of the polymer bind the reagent ions, an increase in Hg^{2+} concentration increases the local Hg^{2+} concentration in the polymer domains and thus accelerates the reaction of bound $Co(NH_3)_5Cl^{2+}$. However, once the polyanions are saturated with reagent ions, further Hg^{2+} addition displaces bound $Co(NH_3)_5Cl^{2+}$, and the reaction rate decreases.

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(5) W. Kern, W. Harold, and B. Scherlag, *Makromol. Chem.*, 17, 231 (1956).

(6) T. J. Painter, *J. Chem. Soc.*, 3932 (1962).

(7) C. L. Arcus, T. L. Howard, and D. S. South, *Chem. Ind.* (London), 1756 (1964).

(8) I. Sakurada, Y. Sakaguchi, T. Ono, and T. Ueda, *Makromol. Chem.*, **91**, 243 (1966).

(9) C. L. Arcus and B. A. Jackson, *Chem. Ind.* (London), 2022 (1964).

Heterocyclic Studies. XXVII. Tautomerism in the Dihydro-1,2-diazepin-4-one System[1]

Sir:

In the course of rather extensive studies of rearrangements and substitution reactions of the 2,3-dihydrodiazepinone **1**,[2] enolization involving both the N-2 and C-3 protons, leading to the deuterium exchange at C-7 and C-3, respectively, has been observed,[3,4] but no other tautomeric forms were detected. We now report the isolation of a second tautomer of this system and the interconversion of these compounds.

The bicyclic ketone **2** is readily obtained by photocyclization of **1** and reverts to the seven-membered valence isomer in the dark.[5] However, treatment of **2** with base at room temperature gives a third isomer, isolated in about 50% yield. This compound,[6] mp 167–168°, ν_{CO}^{KBr} 1630 cm^{-1}, λ_{max}^{MeOH} 241 (ϵ 12,700), 304 (ϵ 8000), and 386 mμ (ϵ 5100), has been found to be the 1,5-dihydrodiazepinone **4**. The spectral values suggest a multiply unsaturated carbonyl system; a semicarbazone,[6] mp 217°, was obtained. Distinctive evidence for structure **4** was provided by the nmr spectrum, which contained a doublet methyl peak; the H-5 peak was split by both H-3 and H-7 [δ^{CDCl_3} 1.08 (d, *J* = 7 Hz; 3), 3.78 (m; 1), 6.77 (dd, *J* = 4 and 1.6 Hz, in $D_2O \rightarrow$ d, 1.6 Hz; 1), and 7.33 ppm (s; 6); $\delta^{DMSO\text{-}d_6}$ 0.89 (d, *J* = 7; 3), 3.67 (ddq, *J* = 7, 1.6, and 1.6 Hz; 1), 6.97 (d, *J* = 1.6 Hz; 1) 7.25 (d, *J* = 1.6 Hz; 1), and 7.37

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(2) J. A. Moore, *Trans. N. Y. Acad. Sci.*, 27, 591 (1965).

(3) J. A. Moore and E. C. Zoll, *J. Org. Chem.*, **29**, 2124 (1964).

(4) J. A. Moore, H. Kwart, G. Wheeler, and H. Bruner, *ibid.*, 32, 1342 (1967).

(5) W. J. Theuer and J. A. Moore, *Chem. Commun.*, 468 (1965).

(6) Satisfactory analytical values were obtained for all compounds reported.