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Communications to the Editor

Stabilization in Cyclopentadienyl, Cyclopentenyl, and Cyclopentyl Cations

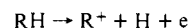
Sir:

Breslow and Hoffman¹ have reported the rate of the silver-assisted solvolysis of 5-cyclopentadienyl iodide to be at least 10^5 times slower than that of cyclopentyl iodide. They concluded that the $c\text{-C}_5\text{H}_5^+$ cation is therefore antiaromatic and exhibits conjugative destabilization. Recent gas-phase experiments in this laboratory provide striking support for their findings. Using an electron monochromator-mass spectrometer combination, described previously,^{2,3} the ionization potentials of cyclopentyl, cyclopentenyl, and cyclopentadienyl radicals, produced in pyrolytic reactions, have been measured as follows (eV): cyclopentyl, 7.47; cyclopentenyl, 7.00; and cyclopentadienyl, 8.41. These electron impact ionization thresholds are probably not more than 0.1 eV above the adiabatic ionization potentials, owing to the energy resolution (0.07 eV fwhm) and high sensitivity available in this apparatus.⁴

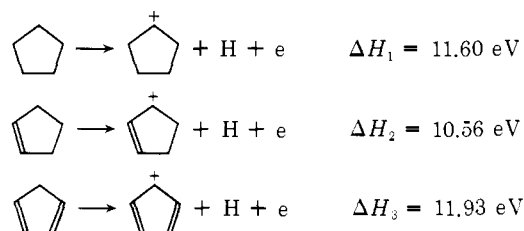
Production of the radicals was carried out in a fused-silica reactor at millisecond contact times³ as follows; cyclopentyl from cyclopentyl methyl nitrite at 350°, cyclopentenyl from 3-allyl cyclopentane at about 800°, and cyclopentadienyl from allyl phenyl ether. In the latter reaction the phenoxy radical produced in the primary bond scission decomposed further to CO + cyclopentadienyl radical⁵ at about 950°.

The heats of formation of the neutral radicals are reasonably well-established as follows (kcal/mol): cyclopentyl, 24.4;^{6,7} cyclopentenyl, 37.8;⁸ and cyclopentadienyl, 60.9 ± 1.2 .⁹ Combined with the ionization potentials given above, these give the following ionic heats of formation (kcal/mol): $c\text{-C}_5\text{H}_9^+$, 197; $c\text{-C}_5\text{H}_7^+$, 199; and $c\text{-C}_5\text{H}_5^+$, 255. These values are to be preferred to those derived from dissociative ionization thresholds, since they correspond to ionic structures of known identity and are probably good to within ± 3 kcal/mol.

The relative stabilization of the three cations is most easily compared by reference to enthalpies of the general reaction



calculated from $\Delta H_f(\text{R}^+)$ and standard heats of formation¹⁰ of the hydrocarbons RH. The corresponding reactions are given below, together with the enthalpies calculated from the present data. It can be seen that while the intro-



duction of one double bond into the C_5 ring brings about a stabilization of 1.04 eV, the second double bond destabilizes the cyclopentenyl cation by 1.37 eV. The $c\text{-C}_5\text{H}_5^+$ ion is consequently destabilized by 0.33 eV (7.6 kcal/mol) with respect to the cyclopentyl cation. This is in close agreement with the solvolysis rate difference of 10^5 found by Breslow and Hoffman,¹ which corresponds to a difference in transition state energies of 7 kcal/mol.¹¹

A fuller account of these results will form part of a later publication.¹²

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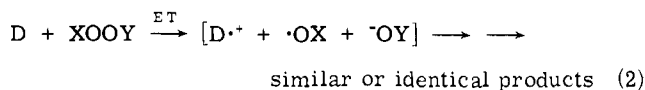
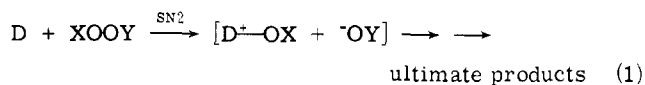
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Radical Production from the Interaction of Closed Shell Molecules. II. The Reaction of Organic Sulfides with *tert*-Butyl Peroxybenzoates¹

Sir:

In recent years it has become clear that a number of the reactions in which nucleophiles react with substrates to give substitution products actually proceed by a chain mechanism involving radicals and radical ions.² In this context, the reactions of nucleophiles (donors) with peroxidic substrates provide a lode of rich variety for study; these reactions can involve either an SN2 reaction (eq 1) or an electron transfer (ET) process (eq 2). Many peroxide-nucleo-



phile reactions which involve an SN2 mechanism are known,³ but very few ET reactions of peroxides have been proposed.

Recently ET reactions have been postulated for the interaction of diphenylhydroxylamine with benzoyl peroxide (BPO)^{4a} and alkyllithium and Grignard reagents with alkyl peroxides.^{4b} In these systems, the leakage of radicals from a seemingly nonradical reaction has been interpreted as an important clue that an ET mechanism is involved.

Distinguishing between SN2 and ET paths is subtle and can be very difficult. For example, in 1950 Horner⁵ postulated that the rapid radical production which results from the reaction of dimethylaniline (DMA) with BPO results from an ET mechanism. In 1957 in his book, Walling⁶ dismissed this possibility and proposed that the DMA-BPO reaction is a normal SN2 process, and that radicals arise from the homolysis of the ammonium salt, $\text{BzO}^- + \text{NMe}_2\text{Ph}$, which is the first intermediate in the ionic displacement process.^{7,8} Horner later partially recanted⁹ and suggested that both ET and an SN2 reaction (followed by homolysis) are responsible for the radical production observed. Despite the fact that research published by several groups in recent years appears to support Horner's original ET mecha-

nism,¹⁰ most of the critical reviews of the DMA-BPO system ignore ET and continue to formulate the DMA-BPO reaction as an SN2 process.¹¹ Clearly, ET reactions of peroxides are not at all easy to establish, and further studies are needed.

We previously reported on the reaction of sulfides with benzoyl peroxide, a process which does *not* produce radicals.^{3c} We now describe the superficially similar reaction of sulfides with *tert*-butyl peroxybenzoates (TBP's) which *does* lead to radicals and for which we propose an ET mechanism.¹² This system is of interest in comparison both with the BPO system and also with *ortho*-mercapto-substituted TBP, studied by Martin, *et al.*^{13,14}

The rate of decomposition of TBP in sulfide solutions can be written as in eq 1 where k_H is the rate constant for homolysis and k_S and k'_S are the second-order and pseudo-first-order rate constants for the sulfide-TBP reaction. The fraction of the bimolecular, assisted process that leads to radicals is calculated by comparing the rates of peroxide and scavenger disappearance. (The TBP disappearance was monitored using the peroxide infrared band at 1758 cm^{-1} ; styrene^{3c} or galvinoxyl in limiting¹⁵ or excess¹⁶ concentration were used as scavengers.)

$$\frac{-d[\text{TBP}]}{dt} = k_H[\text{TBP}] + k_S[\text{R}_2\text{S}][\text{TBP}] = (k_H + k'_S)[\text{TBP}] \quad (1)$$

Table I gives the data; the last three columns give the per cent radical production. Despite the lack of precision in these small values,^{17,18} it is clear that the interaction of sulfides with TBP derivatives does produce radicals. Conservatively, averaging all the data in the last three columns, $2.3 \pm 1.5\%$ of the bimolecular interactions produce radicals.¹⁹

It is important to establish that the radicals we observe do not arise from homolysis of an intermediate produced in an SN2 process. It is clear that species such as BzOS^+Me_2 or $\text{BzOS}(\text{Me})=\text{CH}_2$,²⁰ which can be formed from $\text{TBP} + \text{Me}_2\text{S}$ by SN2 processes, do not produce radicals since the BPO-Me₂S system does not form radicals.^{3e,21} Homolysis of *t*-BuOS⁺Me₂ was excluded by showing that MeOS⁺Me₂, synthesized independently,²² initiates the polymerization of styrene too slowly to be responsible for radical production in the Me₂S-BPO system.

The products (gas chromatographic analysis) from reaction of 1 *M* dimethyl sulfide with TBP at 80° in CCl₄ containing 0.2 *M* styrene (to eliminate induced decomposition) are 90% *t*-C₄H₉OH, 96% CH₃SCH₂OCOC₆H₅ (BOMS),^{3e,23,24} six unidentified compounds in less than 1% yield, and no DMSO, PhCO₂H, or *tert*-butyl benzoate. Without styrene the products are 90% *t*-C₄H₉OH, 40–50% C₆H₅CO₂H, and 50–60% BOMS.

Equations 2a, 2b, and 3 present a generalized mechanism

Table I. The Reaction of Dialkyl and Aryl Alkyl Sulfides with Substituted *tert*-Butyl Peroxybenzoates^a

Substituent ^b	10 ⁷ k_H , ^c sec ⁻¹	10 ⁷ k'_S , ^d sec ⁻¹	Assisted path, ^{d,e} %	Radicals from assisted path, % ^h		
				Styrene	Lim ^f Gal	Excess ^f Gal
p-CH ₃ O	10	89	90	3.5	3.5	
H	8.8	146	94	2.9	0.6	
p-Cl	4.2	334	99	0.7	0.6	
p-NO ₂	2.9	1550	100	2.3	0.9	3.5
3,5-(NO ₂) ₂	1.1	13400	100			4.7
Rho ^g	-0.29 ± 0.05	+1.34 ± 0.03				

^a At 80° in CCl₄. ^b In perester. ^c Unimolecular homolysis, extrapolated from higher temperatures; 0.2 *M* styrene present to reduce induced decomposition. ^d In 1 *M* methyl sulfide in CCl₄. ^e Per cent of total reaction which is bimolecular. $100k'_S/(k_H + k'_S)$. ^f Limiting or excess galvinoxyl. ^g Hammett ρ value. ^h Calculated as the ratio of the rates of scavenger disappearance in R₂S-containing solutions (corrected for scavenger loss due to first-order homolysis) to scavenger disappearance in non-sulfide solutions, divided by the ratio of the rates of TBP disappearance in sulfide solutions to non-sulfide solutions.^{1b, 3e, 13a}